Questions for *Chemistry and the Environment*

Chapter 1 The Earth

Review

1. What measurements have been used to calculate the Earth's age? What is the Earth's age?
2. What is the internal structure of the Earth?
3. Consider Figure 1.1. Where did the water in the oceans come from?
4. The distribution of elements in the universe is very close to that of the material produced by the Big Bang. What is the mass fraction of hydrogen in the universe? (Cf. mole fractions, p. 5.)
5. Why is the distribution of elements on the Earth different from that of Universe? Discuss the processes that gave rise to the Earth.
6. Which planets have a composition similar to Earth? Why?
7. Look at Figure 1.4. How has the oxidation state of the atmosphere changed with time? What caused this change?
8. Why don't *S* waves propagate in liquids? Why are *LR* waves typically more intense than *P* and *S* waves?
9. What is the significance of Moho and how is it located?
10. Where does Rn come from? Why does Rn exposure depend on geology and building materials?
11. Why do $\delta(D)$ and $\delta(^{18}O)$ change in rainwater from different locations?
12. Based on the Wilson cycle, would you predict volcanoes and earthquakes in Denmark? Iceland? Australia? New Zealand? Explain the mechanism.
13. During which geological period did today's deposits of coal and oil form?

Exercises

14. *a* Calculate the average density (g/ml) of the planets Mercury and Jupiter. The mean radius of Mercury is 2.4397 Mm and its mass 330.2 Yg. The mean radius of Jupiter is 69.911 Mm and its mass 1898.6 Yg.
    b Compare this to the densities of the terrestrial planets found in Table 1.3. Comment.
15. Write a balanced chemical reaction for the oxidation of pyrite in wet air. (Pyrite, FeS_2, is the disulfide of iron(II).)
16. Give three different examples of how the oxidation of a non-metallic element in air produces an acid. Elements are oxidized when they are exposed to the atmosphere; what is the balancing reduction reaction?
17. The atmosphere of Venus is 96.4 % CO_2. If we assume young Earth had a similar atmosphere, where is this CO_2 found today? Next, answer again but substitute 'Mars' for 'Earth'.
18. See Table 1.6. Assuming that the density of biota is 1 g/ml, what is the volume of Earth's biota in km^3 ?
19. What is the average pressure at the bottom of the ocean? The maximum pressure at the bottom of the ocean?

Hint. See data in Table 1.7, assume the density of water is not affected by pressure and use eq 2.78.

20. Consider Figure 1.7. Why are oxides found primarily in the upper regions, and why does iron partition to the inside?
21. Geothermal power. Consider eqs 1.7 and 1.8. About how deep should one drill in continental bedrock to generate steam for geothermal energy? What would the pressure be at this depth? Why is Iceland a good location for geothermal energy? What is the source of the energy?
22. How much of the ^{40}K originally present when Earth formed is still here today? Cf. Table 1.12, consider eq 1.10 and use eq 2.56. How much Ar has been produced by this process? Can this source explain the Ar found in the atmosphere today? Calculate the amount of Ar in the modern atmosphere using the mole fraction of Ar and the amount of air in the atmosphere found in Table 3.18.
23. What is the $\delta(^{18}O)$ of rainwater orginating from the sea surface at 3 ºC and 35 ºC? Cf. eq 1.16.
24. Why are plants depleted in ^{13}C relative to atmospheric CO_2?
25. The mass of the Earth is 5976 Yg and its volume 1083 Mm^3. Calculate its average density in $g\,cm^{-3}$.
26. Write the balanced chemical reactions for photosynthesis and respiration. What effect have these processes had on the chemistry of the lithosphere, hydrosphere and atmosphere?
27. Explain the trends and patterns found in Figure 1.2.
28. In the Goldschmidt geochemical classification of the elements (Figure 1.3), why is the volatility of the element considered in some cases, while in other cases the volatility of the oxide is most important? Why is volatility important?
29. Is the Earth's atmosphere primary or secondary? What evidence supports your conclusion?
30. Draw a figure showing Eratosthenes' method for calculating Earth's radius. How accurate is his result?
31. Ar is found in the lattice of some minerals. How did it get there?
32. Would you expect coal to be depleted or enriched in ^{13}C? Why?
33. What is the significance of the Curie temperature for the residual magnetism observed on the ocean floor?
34. There was an explosion of plant growth in the Carboniferous age that produced the coal, oil and gas deposits found on Earth today. However, atmospheric CO_2 and oceanic carbonate levels were largely stable during this era. How could this be?
35. Write formula, colour and state of aggregation at 300 K, 1 bar, for naturally occuring oxides of *a* carbon, *b* nitrogen and *c* sulfur.
36. Calculate *a* the mass and *b* the density of the Earth from the following data

    Mean radius (sphere), $r_E = 6371$ km
    Standard acceleration of gravity, $g_n = 9.80665\ \mathrm{m\,s^{-2}}$ (defined)
    Gravitational constant, $G = 6.67259\times10^{-11}\ \mathrm{m^3\,kg^{-1}\,s^{-2}}$
37. Calculate the radius of the Earth from Eratosthenes' data.

Questions for *Chemistry and the Environment*

Chapter 2 Environmental dynamics

Exercises

38. Give an SI-unit for the physical quantities mass flux and amount flux.

39. Give an SI-unit for the physical quantities amount flux and amount flux density.

40. Consider a column of water, density 1.00 g / ml, in a gravitational field with an acceleration of 9.806 m s^{-2}. What difference of height of the water column corresponds to a pressure difference of 1 bar?

41. Assume that seawater is an aqueous solution of 0.6 M NaCl with the density 1.02 g / ml at 10 °C. Calculate *a* the osmotic pressure and *b* the osmotic head relative to pure water. Cf. eq 2.85.

42. 'Darcy' is the name of a non SI unit characterizing a rock's permeability to fluids, *e.g.* natural gas, oil or water. A Darcy is defined as the permeability μ_p resulting in a flux density of $\boldsymbol{J}$ = 1.00 ml s^{-1} cm^{-2} for a fluid with density ρ = 1.00 g ml^{-1} and viscosity η = 1.00 cP given a pressure gradient of $\boldsymbol{grad}\,p$ = 1.00 atm cm^{-1}.

a Explain how eq 2.95 leads to the expression

$$\boldsymbol{J} = -\mu_\mathrm{p}\frac{\rho}{\eta}\,\boldsymbol{grad}\,p$$

b The unit milliDarcy is in general use. Verify eq 2.98.

c Use the values defining 1 Darcy to calculate the hydraulic conductivity, μ_D, (cf. eq 2.96) which corresponds to 1 milliDarcy.

43. Estimate the molar entropy of vaporization $\Delta_\mathrm{vap}S(T_\mathrm{b})$ using the boiling point T_b and the molar enthalpy of vaporization $\Delta_\mathrm{vap}H(T_\mathrm{b})$ for the following compounds

1	benzene, C_6H_6	T_b = 353 K	$\Delta_\mathrm{vap}H$ = 30.7 kJ/mol
2	toluene, $C_6H_5CH_3$	T_b = 384 K	$\Delta_\mathrm{vap}H$ = 33.2 kJ/mol
3	1,4-dichlorobenzene, $C_6H_4Cl_2$	T_b = 447 K	$\Delta_\mathrm{vap}H$ = 39.7 kJ/mol
4	aniline, $C_6H_5NH_2$	T_b = 458 K	$\Delta_\mathrm{vap}H$ = 44.5 kJ/mol

a Use the left hand side of eq 2.183.

b Use Kistiakowsky's relation, eq 2.184.

c Compare with Trouton's relation and discuss the discrepancies.

44. Estimate the vapor pressure p(300 K) of species *1* and *2* in problem 43 from the normal boiling point T_b and the molar enthalpy of vaporization $\Delta_\mathrm{vap}H(T_\mathrm{b})$.

a Integrate the Clausius-Clapeyron equation, eq 2.182, cf. the van't Hoff equation, eq 2.175, and compare with the experimental values:

1. 13.8 kPa *2.* 3.7 kPa

45. Data for 1,4-dichlorobenzene, B, from ref. 129, **16**-24.

M = 147.00 g/mol; θ_m = 53 °C; θ_b = 174 °C; s_B = 0.08 g/l (solubility in water, 25 °C);

p_B = 0.3 kPa (vapor pressure, 25 °C); $k_\mathrm{H,\,B} = 1.5\times10^{-3}$ bar m^3 / mol.

a Use eq 2.205 to assess whether or not the data are consistent.

b Calculate the partial pressure of B over a saturated solution of B(s) in water at 25 °C using $k_{\mathrm{H,\,B}}$.

Ostwald's absorption coefficient $K_{\mathrm{O,\,B}}$ is defined as the constant of Nernst's distribution law, the middle expression of eq 2.209, $K_{\mathrm{O,\,B}} = c_{\mathrm{B}}{}^{\mathrm{g}} / c_{\mathrm{B}}{}^{\mathrm{l}}$, assuming ideal conditions.

c Calculate $K_{\mathrm{O,\,B}}$ at 25 °C.

46. Consider the following octanol-water partitioning coefficients from ref. 129, **16**.

B	benzene	toluene	1,4-dichlorobenzene	aniline	hexane
$K_{c,\mathrm{B}}^{\mathrm{ow}}$	135	263	3311	7.9	10^4

Give a qualitative explanation of the variation of the partition coefficients.

Questions for *Chemistry and the Environment*

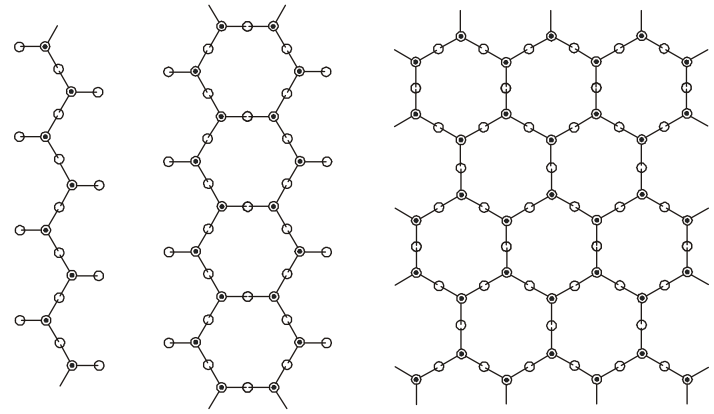
Chapter 3.1 The Lithosphere

Review

47. Name and define five spheres.
48. Define 'rock' and 'mineral'.
49. What element makes up 90 % of the volume of the rocks in the crust?
50. Name the 10 most common elements in the crust without looking at the table.
51. Explain the bonding patterns for oxygen in silicates.
52. What cations are observed in olivine?
53. What is diagenesis and what type of rocks does it help form?

Exercises

54. Which of the minerals in Table 3.4 are carbonates? silicates? oxides?
55. Give an example of a reaction that could be used to permanently store CO_2 in mineral form in the lithosphere.
56. Consider the minerals quartz, albite, orthoclase and anorthite.
    a Write the chemical formula for each mineral.
    b Explain the isomorphic substitution seen in the series.
57. Consider the weathering of rocks.
    a List the chemical agents responsible for the weathering of the minerals found in Table 3.11.
    b Which of the reactions exchange protons for metal ions?
    c Consider the equilibrium $CO_2 + H_2O \rightleftharpoons H_2CO_3\,(aq) \rightleftharpoons H^+ + HCO_3^-$. The reactions eq 3.5 and eq 3.6 are related to the hydrolysis reactions shown in Table 3.11. Which ones?
    d Write how hydrolysis reaction d (*e.g.* pyroxene) in Table 3.11 could be accomplished using CO_2 and H_2O instead of H^+.
58. What is the main source of energy to the surface of Earth? What is the main source of energy to the core? How much energy does each of these two sources provide, in units of $W\,m^{-2}$?
59. Give two examples of isomorphic substitution in minerals.
60. Draw the 3D structure of three units of a single strand polymer silicate. Viewed from a certain angle, the anions of pyroxenes, amphiboles and phyllosilicates all look the same. How are they different?
61. How is granite different from basalt, chemically, physically, geographically?
62. Name two biogenic sedimentary rocks.
63. Write structural formulas according to the VSEPR-rules for the anions in
    a the nesosilicates (orthosilicates), $[SiO_4^{4-}]$
    b the sorosilicates (disilicates), $[Si_2O_7^{6-}]$
    Deduce empirical formulas for the silicate ion in *c* the pyroxenes (single strand chain anions), *d* the amphiboles (double strand chain anions), and *e* the phyllosilicates (sheet structure of the anions) from the structural formulas in the Figure.



Silicate ions of some minerals
Inosilicates: Pyroxene ('chain silicate', left) and amphibole ('band silicate', middle).
Phyllosilicate ('leaf silicate', right).

64. Name the three main types of rocks and describe briefly how they are formed.
65. Name the collection of chemical processes by which an unconsolidated sediment is converted into coherent sedimentary rock.
66. Explain briefly why silicates containing aluminium in place of some silicon belong to the rock-forming minerals.
67. Explain what is meant by an acid, a basic and an ultra basic igneous rock.
68. During cooling of magma the minerals crystalize in the sequence: olivine, pyroxene, amphibole, mica, quarz. Which contain water or hydroxide?
69. Explain what is meant by the phrase: 'Gabbro is a basic rock'.
70. Explain what is meant by the phrase: 'Rhyolite is an acidic rock'.
71. Explain briefly the classification: Igneous rock, sedimentary rock, metamorphic rock.
72. Explain the concept 'isomorphic substitution' and discuss the olivines forsterite Mg_2SiO_4 and fayalite Fe_2SiO_4.
73. Explain the concept 'isomorphic substitution' and discuss the plagioclases albite $NaAlSi_3O_8$ and anorthite $CaAl_2Si_2O_8$.
74. Quantitative analysis of an anorthite from Sittampundi, India, showed the composition: $Ca_{3,742}Sr_{0,103}Na_{0,079}[Fe^{III}_{0,011}Al_{7,898}Si_{8,126}O_{32}]$.
    Based on this specimen, answer the following questions:
    - *a* What is meant by isomorphic substitution?
    - *b* What is the coordination number of Si, Al and Fe?
    - *c* Explain whether the formula $(Ca, Sr, Na)[(Fe^{III}, Al, Si)AlSi_2O_8]$ represents the composition of the feldspar.
75. A sample of bauxite from Southern France consists of a mixture of boehmite, AlO(OH), and goethite, FeO(OH), in the mole ratio of 4:1.
    - *a* What color is the bauxite when observed from a distance?
    - *b* Which ion gives rise to the color?

Questions for *Chemistry and the Environment*

Chapter 3.2 The Hydrosphere

Review

76. Why is the vapor pressure of heavy water different from the vapor pressure of light water?
77. Calculate the amount concentration of water in water assuming a density of 1 g/ml.
78. What is the conjugate acid of water? The conjugate base?
79. Why doesn't the actual concentration of water, [H_2O], appear in the equilibrium expression, eq 5.4?
80. Explain how chemical oxygen demand and biological oxygen demand are determined. Is there a difference in the species produced by chemical *vs.* biological oxidation?

Exercises

81. Consider the hydrological cycle shown in Figure 3.3.
    a What is the lifetime of water in the oceans with respect to evaporation?
    b According to the figure, the evaporation of water from the ocean uses 1 YJ/a. Show that this is correct.
    c Compare the energy released into the atmosphere through condensing water to the annual energy consumption of humanity, Table 8.3.
82. Consider river water and sea water.
    a Compare the dominant salts in river and sea water, and the pH. Comment on the differences. (Cf. Tables 3.13 and 3.14).
    b Calculate the ionic strength (eq 5.56) of sea water and river water (to simplify, use only the most important 3 or 4 cations/anions). How much higher is the ionic strength of the Dead Sea relative to the Danish Straits (Øresund)?
83. Define *a* the hardness of water, *b* the temporary hardness of water and *c* the permanent hardness of water.
84. Calculate the (temporary) hardness of water that contains 1.5 mmol/l $Ca(HCO_3)_2$ and 0.5 mmol/l $Mg(HCO_3)_2$. Is this water hard or soft?
85. Give more than two examples of acid oxides, and of basic oxides.
86. Show that an annual rainfall 730 mm/a corresponds to the average mass flux density $2\,\mathrm{kg\,m^{-2}\,d^{-1}}$.
    Hint: Show that $J = 1\ \mathrm{kg\ m^{-2}\ a^{-1}}$ corresponds to $u = J/\rho = 1$ mm/a.
87. Based on Figure 3.3, what fraction of rain falls on land? How does this compare to the fraction of Earth's surface covered by land? Assuming the density of rainwater is 1 g/ml, what is the average annual rainfall on the Earth's surface?
88. Write the balanced reaction equation for the complete microbial oxidation of the lipid glyceryl stearate $C_3H_5O_3(OC{\cdot}C_{17}H_{35})_3$.
89. Write a balanced reaction equation for the oxidation of cysteine, $CH_2(SH){\cdot}CH(NH_2){\cdot}COOH$, by potassium dichromate in sulfuric acid.
90. Define the mass fraction w_{BOD} of an environmental water.

BOD $\hat{=}$ 'biological oxygen demand'.

91. Describe with necessary detail how the mass fraction w_{BOD} is measured.

92. Define the mass fraction w_{COD} of an environmental water.
COD $\hat{=}$ 'chemical oxygen demand'.

93. Describe with necessary detail how the mass fraction w_{COD} is measured.

94. The water in a sewer was analysed for salinity and biological oxygen demand giving: $w_{\mathrm{salinity}} = 0.010$ and $w_{\mathrm{BOD}} = 320\times10^{-6}$. Describe how such results are obtained in such a way that can be understood by a fellow student.

95. Chemical oxygen demand was determined by weighing an appropriate amount of the aqueous sample followed by refluxing with sulfuric acid containing potassium dichromate (and silver sulfate as catalyst). The surplus of dichromate was determined by iodometry (or alternatively, titration with iron(II)sulfate). Write the reaction equations, and note that ammonium is not oxidized.

96. A sample of 200.00 g of sewage was treated with 400 mg of potassium dichromate as discussed in problem 95. The surplus dichromate was titrated using 21.00 ml of 0.1000 M iron(II) sulfate. Calculate w_{COD}.

97. In the design of a wastewater treatment plant the organic matter in the sewage was assumed to have the composition $C_{18}H_{19}O_9N$. This waste can be oxidized by aerobic, heterotrophic bacteria in two ways: *a* without and *b* with nitrification. Write balanced reaction equations and find the maximum biological oxygen demand for the two cases.

98. Calculate the maximum biological oxygen demand without and with nitrification for the nine species in Table 3.28.

99. Wastewater from a plant contains glutamate, $^{-}OOC{-}CH_2{-}CH_2{-}CHNH_3^{+}{-}COO^{-}$. The concentration is 1.5 kg/m^3 and the flux of water is 300 m^3/d.
a Calculate w_{COD} in the wastewater.
The water is led into a biological wastewater treatment plant which does not perform nitrification. The plant is assumed to oxidize 70 % of the organic contamination.
b Calculate the amount and the mass of oxygen required per day.

100. A wastewater treatment plant produces biomass, $C_5H_7O_2N$, and carbon dioxide from an organic substrate composed of $C_{18}H_{19}O_9N$, amonium/ammonia and oxygen.
a Suppose that the yield, calculated as the ratio $m(C_5H_7O_2N)/m(C_{18}H_{19}O_9N)$, is 0.5. On this basis, write the reaction scheme. (Note that additional nitrogen must be supplied in order to convert the substrate into biomass.)
b Calculate the yield as the ratio $w_{\mathrm{COD}}(C_5H_7O_2N)/w_{\mathrm{COD}}(C_{18}H_{19}O_9N)$.

101. The biological processes in a water treatment plant that removes phosphate from wastewater may be described by the following brutto processes:

Under aerobic conditions (oxidative environment, oxygen is electron acceptor) phosphate is fixed according to the equation

$$\begin{aligned} &50\,CH_2O + 4\,NH_4^{+} + 5\,H_2PO_4^{-} + 30\,O_2 \rightarrow \\ &\qquad (C_5H_7O_2N)_4(HPO_3)_5 + 29\,CO_2 + HCO_3^{-} + 46\,H_2O \end{aligned} \tag{1}$$

but phosphate can also be fixed under anoxic conditions (oxidative environment, nitrate is electron acceptor; no free oxygen in the system)

$$50\,CH_2O \;+\; 4\,NH_4^+ \;+\; 5\,H_2PO_4^- \;+\; 24\,NO_3^- \;\rightarrow$$
$$(C_5H_7O_2N)_4(HPO_3)_5 \;+\; 5\,CO_2 \;+\; 25\,HCO_3^- \;+\; 12\,N_2 \;+\; 34\,H_2O \qquad (2)$$

On the other hand, under anaerobic conditions phosphate is liberated by a reaction which is chemically equivalent to a hydrolysis.

a Consider wastewater which contains 48 g/m^3 of acetic acid and 9.6 g/m^3 of phosphorous measured as mass of elemental P. Calculate the fraction of dihydrogen phosphate which may be removed according to eq 1.

b Calculate the ratio $w_{COD}((C_5H_7O_2N)_4(HPO_3)_5)/w_{COD}(\text{substrate})$.

c Write the reaction equation for the anaerobic process.

d Explain whether the two processes change the alkalinity in the same way.

Note: This sub-question 101*d* belongs to Chapter 5.1.

102. A sample of wastewater contained the mass fractions $w_P = 21\times10^{-6}$, $w_N = 60\times10^{-6}$ and $w_{BOD} = 296\times10^{-6}$. According to Danish Government regulations (1993) water from a wastewater treatment plant may contain at most $w_P = 1.5\times10^{-6}$, $w_N = 8\times10^{-6}$ and $w_{BOD} = 15\times10^{-6}$.

a Assume the reaction equation

$$5\,CH_2O \;+\; 4\,NO_3^- + 4\,H^+ \;\rightarrow\; 5\,CO_2 + 2\,N_2 + 7\,H_2O \qquad (1)$$

and calculate the mass of saccharide that is necessary in order to reduce w_N from 60 ppm to 8 ppm.

b Suppose that algae are formed according to the reaction scheme:

$$106\,CO_2 + 16\,NH_4^+ + H_2PO_4^- + 108\,H_2O \;\rightarrow$$
$$C_{106}H_{263}O_{110}N_{16}P + 107\,O_2 + 15\,H^+ \qquad (2)$$

Consider a case in which the wastewater to be treated has $w(NH_4^+) \approx 2\ \mu g/kg$ and $w(H_2PO_4^-/HPO_4^{2-}) \approx 50\ \mu g/kg$. Which of the two elements, N or P, will restrict algal growth?

Questions for *Chemistry and the Environment*

Chapter 3.3 The Atmosphere

Review

103. How is the top of the atmosphere defined? What is its name?
104. Why is the troposphere mixed and the stratosphere stable?
105. Calculate the average molar mass of dry air considering the mole fractions of O_2, N_2 and Ar.
106. Does the solubility of gases in water increase or decrease with increasing temperature?
107. What is the density of air at *a.* 1000 mbar? *b.* 100 mbar? *Hint.* Use eq 3.17.
108. Why does water make the troposphere less stable?
109. Describe the circulation of air through the stratosphere.
110. What is the Coriolis force and what effect does it have on atmospheric circulation?
111. Why are the world's great deserts located where they are?

Exercises

112. Write the photochemical reactions that explain why the temperature of the stratosphere increases with altitude.
113. Sea salt aerosol is generated by breaking waves on the ocean. These aerosols fall out of the atmosphere resulting in a scale height of 0.5 km. If the average mass concentration of sea salt aerosol just above the ocean is $10\,\mu g\,m^{-3}$, calculate the total mass of sea salt in the atmosphere. *Hint*: You will need to integrate the barometric equation from an altitude of zero to infinity.
114. *a* The mean pressure of the surface of the Earth is 984 mbar, slightly less than the mean pressure at sea level, 1013 mbar. Use the barometric equation to calculate the mean altitude of the surface above sea level.
    b Calculate the total mass of the atmosphere by considering that $p = F / A$, where p is pressure, F force and A area. The downward force of the atmosphere, by Newton's Law, is the mass of the atmosphere times the acceleration of gravity. The mean pressure can be found above, and the area is the surface area of the earth. Use the average molar mass of the atmosphere to calculate the amount of gas in the atmosphere.
    c Use the amount of gas in the atmosphere and the mole fraction of N_2O (Table 3.19) to calculate the amount and mass of N_2O in the atmosphere.
115. Consider a building that takes in air from outside (100 % relative humidity, –10 °C), and heats it to 20 °C. What is the relative humidity inside the building assuming no other sources of water vapor? (Table 3.15).
116. Consider a cloud at 10 °C and 750 mbar. The mole fraction of SO_2 in the gas phase is 20×10^{-9}, and of CO_2, 380×10^{-6}. What are the concentrations of SO_2 and CO_2 in the water droplets in the cloud? (Cf. eq. 3.13, Table 3.22).
117. Name the two opposing forces that determine the size of the atmosphere.
118. What are the ten most common gasses in the atmosphere?
119. Take the atmosphere of the early earth to be 96 % CO_2 and 4 % N_2. Calculate the scale height (cf. definition in text below eq 2.81) assuming an average atmospheric temperature of 255 K.

How does this compare to the scale height of today's atmosphere?

120. Consider an atmosphere at 20 °C with a water mole fraction of 0.011. What is the relative humidity? (cf. Table 3.21)

121. A bolt of lightning produces the mass fraction $w_{NO} = 100 \times 10^{-9}$ of NO in a cloud. The pressure is 500 mbar and the temperature is 0 °C. What is the concentration of NO in the condensed water phase?

122. Why does the position of the intertropical convergence zone depend on season?

123. Consider Hadley's model of atmospheric circulation. Why is the Polar Cell 'active' and the Ferrel Cell 'passive'?

124. The ratio between the mole fractions of nitrogen and oxygen in the atmosphere is $x(N_2) / x(O_2) = 3.75$. How does this ratio change for air dissolved in fresh water in equilibrium with the atmosphere?

125. Name the four chemical species that are most abundant (mole fraction) in dry atmospheric air.

126. Demonstrate the proposition that in an ideal mixture of gases the mole fraction of a gas, its partial pressure and its volume fraction are proportional.

127. Show that the amount of substance in the atmosphere is approximately 182 Emol.
Hint: Use all the following data: The circumference of the Earth is 40 Mm; the standard acceleration of gravity is $g_n = 9.807$ m s^{-2}; the normal pressure of the atmosphere is 1 bar = 1013 hPa; the molar mass of atmospheric air is 28.96 g mol^{-1}.

128. Assume that the atmosphere contains 354 ppm CO_2 (*i.e.* the mole fraction is 0.354×10^{-3}). Calculate the partial pressure.

129. Explain how the solubility of oxygen in water varies with *a* salinity and *b* temperature.

Questions for *Chemistry and the Environment*

Chapter 3.4 Biota

Review

130. What is the difference between a eukaryote and a prokaryote? What are the classes of eukaryotes?
131. What is the basic chemical formula for (dry) biological tissue? What are the ten most common elements in dry biological tissue?
132. What is humus and what are its fractions?
133. What is diagenesis and why does it occur?
134. Describe the chemical evidence that coal and oil come from biota.
135. Give a balanced reaction equation for the catabolic breakdown of a lipid (Table 3.28) to produce carbon dioxide and water.
136. What inorganic oxidants are used in anaerobic oxidation?
137. Aerobic organisms are most often dominant in an oxygenated environment. Why? (Cf. Table 3.29)
138. Is methanogenesis associated with an increase or a decrease in pH?

Exercises

139. Write a balanced chemical equation for turning humic acid into anthracite by diagenesis.
140. The Gibbs free energy change of eq 3.19 is 478.7 kJ/mol. Assume this energy is obtained by the absorption of four photons of light and calculate their wavelength. How does this compare with the emission spectrum of the Sun (Figure 10.1)?
141. What mass of glucose should a person consume per hour to maintain respiration at 90 W?
142. Give the classification of cells in a human, a tomato plant, a mushroom and a yeast (carbon source, energy source, reduction substrate, type of respiration).
143. An adult human consumes about 90 W. How much energy is this per day?
144. Write the oxidation state of the oxidizing agent before and after reaction for the reactions in Table 3.29.
145. Write the characteristic reaction equations for *a* a respiration and *b* a fermentation.

Questions for *Chemistry and the Environment*

Chapter 4 Chemistry of the atmosphere

Review

146. What three types of process define a chain reaction?
147. What is 'M' and why is it necessary for a three body reaction?
148. Explain Figure 4.1 - where does the original intensity spectrum come from, and why does it change with decreasing altitude?
149. Write the elementary reactions and the net reaction for the oxidation of CO in a high NO_x and a low NO_x atmosphere. Comment.
150. Write the elementary reactions and the net reaction for the oxidation of CH_4 in a high NO_x and a low NO_x atmosphere. (To simplify, assume that all formaldehyde reacts with OH.) Comment.
151. What are the two reactions that terminate the chain reaction for tropospheric chemistry shown in Figure 4.3, thereby reducing its efficiency?
152. Explain how the formation of PAN results in the spread of NO_x through the northern hemisphere.
153. What wavelengths does ozone shield the surface against?
154. Why is $[O_x]$ approximately equal to $[O_3]$?
155. Why is there a temperature inversion in the stratosphere?
156. Write the source reactions of stratospheric HO_x, ClO_x and NO_x.
157. What is the significance of the anticorrelation shown in Figure 4.9?
158. How are HCl and $ClNO_3$ turned into ClO_x in the Antarctic atmosphere?

Exercises

159. Derive eq 4.10 using the steady state approximation. Explain the distribution of OH in Figure 4.2 using this equation. Does the formation of OH result in a decrease of tropospheric ozone?
160. In Figure 4.4, how is it possible that in some circumstances increasing NO_x pollution can lead to less O_3 pollution? In this case, what is the best anti-pollution strategy?
161. Draw the atmospheric degradation schemes for ethane and propane, based on what you know from the degradation of methane. Assume high-NO_x conditions.
162. What is the lifetime of ethene given the following conditions? Which radical is the most important for removing ethene?

Radical 'R'	Concentration / cm^{-3}	Rate constant / $(cm^3\,s^{-1})$
Cl	1.3×10^5	9.3×10^{-11}
O_3	6.2×10^{11}	1.4×10^{-18}
OH	9.5×10^5	9.4×10^{-12}
NO_3	1.1×10^8	2.0×10^{-16}

163. Consider a fog with a liquid water content of $0.05\,g\,m^{-3}$, 298 K, 1013 mbar. The gas phase contains $20\,mg\,m^{-3}$ of SO_2 and the mole fraction 30×10^{-9} of O_3. What fraction of each gas is in the liquid phase? (Cf. Henry's Law constants, Table 4.5)

164. The Chapman Mechanism.
    - *a* Make a figure showing the four reactions in the Chapman mechanism. Circle the 'O_x' compounds. Label two reactions 'fast' and two reactions 'slow'.
    - *b* Use the steady state approximation on O to derive an expression for the ratio $[O]/[O_3]$. Justify the approximation used in eq 4.56.
    - *c* Use the steady state approximation on O_x to derive eq 4.59. Explain how the amount of ozone will change depending on altitude.
    - *d* Discuss Chapman's mechanism: Why does it overpredict O_3 relative to observations in the middle stratosphere? Why does it underpredict O_3 relative to observations in the lower stratosphere?

165. Why can't traditional ClO_x catalytic chemistry explain the Antarctic ozone hole? What reaction cycle does explain it?
166. Compare the effect of CF_2Cl_2 and CF_3CH_2F on the atmospheric environment. Comment on the removal mechanism, lifetime and environmental impact of each.
167. Give an example of an atmospheric unimolecular, bimolecular and termolecular reaction.
168. What is 'actinic flux'? Why is it important?
169. In Figure 4.2, why does [OH] increase above 9 km?
170. Describe the difference in the behavior of NO_x in the troposphere and stratosphere.
171. In Figure 4.3, explain how OH can be converted to an aldehyde and HO_2.
172. What two reactions determine if the atmosphere is 'high NO_x' or 'low NO_x'? What limits ozone formation in each of these conditions?
173. How can air pollution result in whiter clouds? Do these clouds affect climate?
174. Explain the special reactivity of molecular oxygen and give examples of three atmospheric reactions involving O_2.
175. What forces compete to determine if an aerosol remains suspended in the atmosphere or falls to the surface? What forces compete to determine if an aerosol reaches the lungs or deposits in the sinus cavity?
176. Will increasing stratospheric NO_x increase or decrease stratospheric ozone? Consider the reactions of NO_2 with OH and ClO.
177. What is the chemical mechanism of chlorine catalyzed ozone depletion at mid latitudes and in the stratosphere?
178. What are the causes of mid-latitude ozone depletion?
179. Show that 300 DU is equal to 134 mmol m^{-2}. (DU = the non-SI unit "dobson unit".)

Questions for *Chemistry and the Environment*

Chapter 5 Chemistry of the hydrosphere

Review

180. How much does the ion product of water change from 0 to 100 °C? (Cf. Table 5.1)
181. How does the ion product of water change from freshwater to seawater? (Cf. Table 5.1 and Figure 5.1)
182. Describe the 'levelling effect' that water has on the observed strength of aqueous acids and bases. What is the strongest acid available in water solution? The strongest base?
183. What is the chemical form of silicic acid in the ocean? (Cf. Table 5.3)
184. Does the solubility of CO_2 in water increase or decrease with temperature? With the ionic strength of the solution? (Cf. Table 5.5)
185. How can iron at (E, pH) = (0 V, 7) be protected from corrosion? (Cf. Figure 5.11)

Exercises

186. Use the enthalpy change of the dissociation of water (Table 5.2) and the van't Hoff equation (eq 2.175) to check that the data in Table 5.1 are correct at 0 °C and 100 °C. Estimate what the ion product of water would be in a lava at 1000 K.
187. This question will consider speciation diagrams.
    - *a* What is the significance of the maximum in the buffer value at a pH of 4.75 shown in Figure 5.2? What ions are present in the solution at this point?
    - *b* What ions comprise the alkalinity of the system shown in Figure 5.3? What is the alkalinity of the solution at a pH of 7?
    - *c* What is the main phosphate species in each region of Figure 5.4?
    - *d* Draw the speciation diagram for propanedioic acid (malonic acid) $HOOC\text{-}CH_2\text{-}COOH$ and hexanedioic acid (adipic acid) $HOOC\text{-}(CH_2)_4\text{-}COOH$ using the pK_a values from Table 5.4. Draw curves representing the buffer capacity and alkalinity for a 0.1 M solution of each of the two species.
188. Consider Tables 5.15 and 5.16. Why is the point of zero charge lower for gibbsite than for goethite? What is the chemical structure of the surface for kaolinite at pH 9?
189. List the reactions responsible for lines *A*, *B* and *C* in Figure 5.8.
    Consider the areas *A*, *B* and *C* in Figure 5.9. How can soil water extend over such a wide range of potentials, and why does rainwater have such a positive potential and low pH?
190. Consider biological oxygen demand and chemical oxygen demand. Write balanced reaction equations for the breakdown of the species $C_{30}H_{42}O_7N$ described pp. 187-188 for both biological and chemical oxidation. Calculate the biological and the chemical oxygen demand.
191. Consider the pentavalent base $C_{30}H_{38}O_7N_4^-$ described in the text pp. 187-188.
    - *a* What is the isoelectric point for this species? What is the chemical form of each of the functional groups of the main component at this pH?
    - *b* What is the main form of the molecule at pH 7?
    - *c* What soil component does this molecule represent?

192. Explain why samples of soil water, rain water and sea water fall in the regions *A*, *B* and *C* in Figure 5.9.

193. Why is iron(II) mobile in reducing groundwater conditions while $Fe(OH)_3$ is not? (Cf. Figure 5.9).

194. Write a program, *e.g.* using Mathematica, Pascal or Maple, which plots eq 5.55 for $4.5 \leq \mathrm{pH} \leq 9.5$ using data from Table 5.5 ($I = 1$ M; $\theta = 25$ °C).

Questions for *Chemistry and the Environment*

Chapter 5.1 Acid-base chemistry

Exercises

195. Define the ion product of water and explain how it varies with temperature.
196. Define the concept of a buffer solution and give three examples of such solutions.
197. Explain why it may be reasonable to classify 8.5 M hydrochloric acid as a buffer solution.
198. Hypochlorous acid (hydrogen monooxochlorate or monooxochloric acid) is a monovalent acid with the acidity constant 1.0×10^{-7} M. What is the alkalinity of a 0.1 M solution of hypochlorite with pH = 8.5?
199. Write the relevant reaction equations for the natural carbon dioxide - water system.
200. Make a sketch of the titration curve for a carbonate solution titrated by strong acid.
201. Define the alkalinity of natural ocean water containing hydrogen carbonate, boric acid and orthosilicic acid.
202. Consider the analysis of samples of surface water. Explain the change in alkalinity during dropwise addition of 0.01 M solutions of :
    a: HCl, *b*: NaOH, *c*: Na_2CO_3, *d*: $NaHCO_3$, *e*: CO_2, *f*: $AlCl_3$, *g*: Na_2SO_4.
203. The following procedure was used to determine the alkalinity of a sample of surface water, (1) measure pH; (2) Add a known amount of mineral acid to a known volume of the sample; (3) measure pH. Explain the protocol and show how the alkalinity is calculated.
204. The temporary hardness of water is due to calcium and magnesium hydrogen carbonates, cf. Chapter 3.2b.
    a Calculate the hardness of water containing 2 mmol/l $Ca(HCO_3)_2$ and 1 mmol/l $Mg(HCO_3)_2$.
    b Calculate the hardness of water in equilibrium with calcite (without exposure to air).
    c Calculate the hardness of water in equilibrium with calcite and an atmosphere with the partial pressure of CO_2 of 13 hPa.

    Constants at 10 °C: $L(\text{calcite}) = 3.80\times10^{-9}\ \text{M}^2$
    $k_H(CO_2) = 0.054\ \text{M bar}^{-1}$
    $\text{p}K(CO_2 + H_2CO_3) = 6.46$; $\text{p}K(HCO_3^-) = 10.49$
205. Calculate pH in ocean water using the following assumptions: Water, calcite and an atmosphere with a partial pressure of CO_2 of 32 Pa are in equilibrium at 10 °C. Use the necessary constants from problem 204.
206. Consider the reaction equations: prob 101, eq 1; prob 101, eq 2; prob 102, eq 1; prob 102, eq 2; prob 207, eq 1; prob 207, eq 2. These may occur in natural environments either directly as written or via enzymatic processes in microorganisms. For each process state whether the alkalinity will increase, decrease or remain unchanged.
207. A sample of surface water is characterized by an alkalinity of 8.5×10^{-4} M, and pH 9.0. The acidity exponents for carbonic acid are $\text{p}K_{a1} = 6.3$ and $\text{p}K_{a2} = 10.2$.
    a First consider a closed system, *i.e.* no CO_2 exchange with the atmosphere and no precipitation of $CaCO_3$. Further, assume photosynthesis occurs according to

$$\mathrm{CO_2 + H_2O \rightarrow CH_2O + O_2} \qquad (1)$$

What changes in alkalinity and pH would you expect?

b Next, consider an open system and photosynthesis with nitrate assimilation according to the reaction equation

$$\mathrm{106\,CO_2 + 16\,NO_3^- + HPO_4^{2-} + 140\,H_2O \rightarrow C_{106}H_{263}N_{16}O_{110}P + 138\,O_2 + 18\,HO^-} \qquad (2)$$

Over the course of three hours, pH changes to 9.5. Calculate the rate at which carbon dioxide is fixed.

208. Show that

a $$\frac{\mathrm{d}[\mathrm{H}^+]}{\mathrm{d}(-\ln[\mathrm{H}^+])} = -[\mathrm{H}^+]$$

b $$\frac{\mathrm{d}[\mathrm{HO}^-]}{\mathrm{d}(-\ln[\mathrm{H}^+])} = \frac{\mathrm{d}}{\mathrm{d}(-\ln[\mathrm{H}^+])}\left(\frac{K_\mathrm{v}}{[\mathrm{H}^+]}\right) = [\mathrm{HO}^-]$$

c $$\frac{\mathrm{d}\alpha_0}{\mathrm{d}(-\ln[\mathrm{H}^+])} = \alpha_0\alpha_1$$

d Find the condition at which $\frac{\mathrm{d}\beta}{\mathrm{dpH}} = 0$

209. Write a program (*e.g.* Mathematica, Pascal or Maple) that is able to calculate pH, alkalinities and buffer values for aqueous solutions of arbitrary mixtures of two monovalent acid-base pairs. Use this program (or the Mathematica notebook examples of Appendix 2) to solve the following problem:

Calculate pH_c of each of the following four aqueous solutions

a $c_\mathrm{HA} = 0.10\,\mathrm{M}$ and $c_\mathrm{HB} = 0.01\,\mathrm{M}$
b $c_\mathrm{NaA} = 0.10\,\mathrm{M}$ and $c_\mathrm{HB} = 0.01\,\mathrm{M}$
c $c_\mathrm{HA} = 0.10\,\mathrm{M}$ and $c_\mathrm{NaB} = 0.01\,\mathrm{M}$
d $c_\mathrm{NaA} = 0.10\,\mathrm{M}$ and $c_\mathrm{NaB} = 0.01\,\mathrm{M}$

Here HA is trichloroacetic acid, $\mathrm{p}K_\mathrm{a} = 5.0$; HB is *p*-nitrophenol, $\mathrm{p}K_\mathrm{a} = 7.0$; $\mathrm{p}K_\mathrm{w} = 14.0$.

210. Sketch speciation diagrams for the following four divalent acids using only paper and pencil:

a	ethanedioic acid (oxalic acid):	$\mathrm{p}K_{\mathrm{a}1} = 1.3$;	$\mathrm{p}K_{\mathrm{a}2} = 4.3$
b	propanedioic acid (malonic acid):	$\mathrm{p}K_{\mathrm{a}1} = 2.9$;	$\mathrm{p}K_{\mathrm{a}2} = 5.7$
c	butanedioic acid (succinic acid):	$\mathrm{p}K_{\mathrm{a}1} = 4.2$;	$\mathrm{p}K_{\mathrm{a}2} = 5.4$
d	nonanedioic acid (azelainic acid):	$\mathrm{p}K_{\mathrm{a}1} = 4.3$;	$\mathrm{p}K_{\mathrm{a}2} = 5.0$

211. An aqueous solution of ammonia has the mass fraction $w(\mathrm{NH_3}) = 0.25$ and a density of 0.910 g/ml. Calculate the concentrations of ammonia and water.

212. Consider two samples of surface water from the Øresund Strait separating Denmark from Sweden. One sample, denoted **A**, was without color but the other, **B**, was colored by 'yellow matter'. Yellow matter consists of fulvic acids that are colored by the formation of complexes

with iron(III).

Each sample contained the same amounts of dioxygen, chloride and hydrogencarbonate but differed in the concentration of yellow matter, measured by evaporating the samples to dryness.

Winkler's method was used to determine free oxygen. Here the gross reaction is

$$\tfrac{1}{2}O_2 + 2S_2O_3^{2-} + 2H^+ \rightarrow S_4O_6^{2-} + H_2O$$

In an experiment 100.00 ml of sample **A** was equivalent to 1.453 ml 0.1000 M thiosulfate.

a1 Calculate the mass concentration γ of dioxygen.

a2 Explain whether there is a connection between γ and the chemical oxygen demand, w_{COD}.

The density ρ of **A** was $\rho = 1.037\ \mathrm{g\,ml^{-1}}$. The concentration of halides in the samples was determined by potentiometric titration with 0.1002 M $AgNO_3$ in dilute nitric acid. In an experiment 3.00 ml of **A** required 8.03 ml of the silver nitrate solution. Assume that the concentration of halide is only due to NaCl.

b1 Calculate the concentration of chloride.

b2 Calculate the salinity.

The alkalinity A of **A** was determined by acidimetric titration at 10 °C: 100.00 ml required 1.83 ml of 0.1007 ml HCl solution. Suppose that the alkalinity is only due to hydrogencarbonate.

b3 Calculate the alkalinity.

Sample **B** contained 6.523 $\mathrm{g\,l^{-1}}$ of yellow matter which (after detailed analytical work) was shown to have the average composition $C_{132}H_{179}O_{95}N_5SFe$, $M = 3441\ \mathrm{g\,mol^{-1}}$.

c1 Write the reaction equation for the complete oxidation of **B** with dioxygen, the products being CO_2, NO_3^-, HSO_4^-, H^+, Fe_2O_3 og H_2O.

c2 Calculate the chemical oxygen demand of **B**, *i.e.* the mass of oxygen used for the oxidation of all yellow matter in one liter of the seawater sample.

Constants. At 10 °C and given the system's ionic strength the acidity constants of carbonic acid are $K_{a1} = 10^{-6.31}\ \mathrm{M}$ and $K_{a2} = 10^{-10.15}\ \mathrm{M}$ and the ion product of water $K_w = 10^{-14.73}\ \mathrm{M}^2$.

Chapter 5.2 Coordination chemistry

Exerscices

213. Write reaction equations to illustrate what is meant by the term 'amphoteric metal hydroxide'.
214. Which of the following metal hydroxides are amphoteric: LiOH, NaOH, KOH, $Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$, $Zn(OH)_2$, $Cd(OH)_2$, $Hg(OH)_2$, $Al(OH)_3$, $Fe(OH)_2$, $Fe(OH)_3$, $Cu(OH)_2$?
215. Give a systematic name of the following species: *a*: Na^+, *b*: Ca^{2+}, *c*: $Al(H_2O)_6^{3+}$, *d*: $ZnCl_4^{2-}$, *e*: $HgCl_2(aq)$, *f*: $HgCl_4^{2-}$, *g*: SO_4^{2-}, and explain when and why the term "ion" is part of the name.
216. Hexaaquaaluminium(3+) is an acid almost as strong as acetic acid. Write *a* the reaction equation that shows this and *b* the definition of the acidity constant.
217. Sketch speciation diagrams for the following complex systems in aqueous solution:

silver(I) - ammonia	$\lg\{K_{c1}/\mathrm{M}^{-1}\} = 3.6$;	$\lg\{K_{c2}/\mathrm{M}^{-1}\} = 3.9$
silver(I) - chloride	$\lg\{\beta_1/\mathrm{M}^{-1}\} = 3$;	$\lg\{\beta_2/\mathrm{M}^{-2}\} = 5$;
	$\lg\{\beta_3/\mathrm{M}^{-3}\} = 6$;	$\lg\{\beta_4/\mathrm{M}^{-4}\} = 6$;
lead(II) - bromide	$\lg\{\beta_1/\mathrm{M}^{-1}\} = 1.5$;	$\lg\{\beta_2/\mathrm{M}^{-2}\} = 2.6$;
	$\lg\{\beta_3/\mathrm{M}^{-3}\} = 3.5$;	$\lg\{\beta_4/\mathrm{M}^{-4}\} = 3.5$;
mercury(II) - ammonia	$\lg\{\beta_1/\mathrm{M}^{-1}\} = 8.8$;	$\lg\{\beta_2/\mathrm{M}^{-2}\} = 17.4$;
	$\lg\{\beta_3/\mathrm{M}^{-3}\} = 18.4$;	$\lg\{\beta_4/\mathrm{M}^{-4}\} = 19.1$;

The acidity constant is $pK_a(NH_4^+) = 9.3$, the ion product of water $pK_w = 14$, and the solubility products: $L(AgCl) = 10^{-10}\ \mathrm{M}^2$ and $L(PbBr_2) = 10^{-5.7}\ \mathrm{M}^3$.

218. Humus was extracted from a soil sample using 0.5 M NaOH. 0.5 M HCl was then added dropwise until the pH reached a value of one. Humic acids were thereby precipitated, with an average composition $C_{187}H_{186}O_{89}N_9S$ ($M = 4.016\ \mathrm{kg\,mol^{-1}}$). The precipitate contained the following functional groups: alcohols, R–OH; phenols, Ar–OH; carboxylic acids, –COOH; imines, =NH; sulfides, –SR; thiols, –SH. The cation exchange capacity was found to be $b_{CEC} = 6.5\ \mathrm{mol\,kg^{-1}}$ (dry mass).

a Calculate w_{COD}(humic acid) for a standard dichromate titration, cf. p. 121.

A truck garden produced $125\ \mathrm{m^3}$ of wastewater containing $1.2\ \mathrm{kg\,m^{-3}}$ of a pollutant with the average composition $C_{187}H_{186}O_{89}N_9S$. The wastewater was treated in a facility which oxidized carbon (→ carbon dioxide) and sulfur (→ sulfate) but not nitrogen; in all only 70 % of the pollutant was oxidized.

b Calculate the volume of atmospheric air that was consumed by the process. (Air: $x(O_2) = 0.21$, $\theta = 15\ °C$)

Soil retains Fe(III), Pb(II), Cd(II) and Hg(II).

c For each metal ion, state which of the functional groups present in the system has the greatest constant of formation.

Questions for *Chemistry and the Environment*

Chapter 5.3 Electrolytic properties

Exercises

219. Write balanced reaction equations that describe the natural iron-water system.
220. Describe using text (color of solutions and precipitates, etc.) and reaction equations what happens when a surplus of strong base is slowly added (dropwise) to an acidic solution of iron(II) sulfate.
221. Describe using text (color of solutions and precipitates, etc.) and reaction equations what happens when a surplus of strong base is slowly added (dropwise) to an acidic solution of iron(III) sulfate.
222. Describe using text (color of solutions and precipitates, etc.) and reaction equations what happens when a surplus of aqueous ammonia is slowly added (dropwise) to an acidic solution of iron(II) sulfate.
223. Describe using text (color of solutions and precipitates, etc.) and reaction equations what happens when a surplus of aqueous ammonia is slowly added (dropwise) to an acidic solution of iron(III) sulfate.
224. Describe using text (color of solutions and precipitates, etc.) and reaction equations what happens when a surplus of strong base (NaOH) is slowly added (dropwise) to an acidic solution of aluminium sulfate. Give a systematic names of all ions and precipitates.
225. Describe using text (color of solutions and precipitates, etc.) and reaction equations what happens when a surplus of aqueous ammonia is slowly added (dropwise) to an acidic solution of aluminium sulfate.
226. The following electrode reactions describe processes that occur in acidic humus containing soils (here given using standard electrode potentials and the systematic names of the oxidized species)

1 $\mathrm{Fe(phen)_3^{3+} + e^- \rightleftharpoons Fe(phen)_3^{2+}}$ $E° = +1.12$ V
tris(orthophenantroline)iron(III)

2 $\mathrm{Fe(H_2O)_6^{3+} + e^- \rightleftharpoons Fe(H_2O)_6^{2+}}$ $E° = +0.77$ V
hexaaquairon(III)

3 $\mathrm{Fe(ox)_3^{3-} + e^- \rightleftharpoons Fe(ox)_3^{4-}}$ $E° = +0.02$ V
tris(oxalato)ferrate(III)

4 $\mathrm{Fe(edta)^- + e^- \rightleftharpoons Fe(edta)^{2-}}$ $E° = -0.12$ V
(ethylendiaminetetraacetato)ferrate(III)

Consider four solutions, each containing one of the redox pairs in equal concentration, 1 mmol/l. Explain your answers to the following three questions:

a Which solution is most oxidizing?
b Which solution is most reducing?
c Explain - including essential experimental details - how such electrode potentials are measured.

227. The standard electrode potential for reduction of nitrate into ammonium is

$$NO_3^- + 10H^+ + 8e^- = NH_4^+ + 3H_2O \qquad E^\circ = +665\,\mathrm{mV}$$

and the acidity exponent of ammonium is pK = 9.22.

Write down Nernst's equation:

a1 find the slope $dE/d\,\mathrm{pH}$

a2 calculate the electrode potential E'°, *i.e.* the potential at pH 7.0, 25 °C, 1 bar.

Write down the electrode reaction at pH 11 and

b1 determine the electrode potential under these conditions.

228. Draw the Pourbaix diagram (E-pH diagram) of the naturally occuring oxo-species of As(III) and As(V) in aqueous solution. Data: eqs 9.34, 5.73 and 5.74.

Questions for *Chemistry and the Environment*

Chapter 6 Chemistry of the pedosphere

Review

229. The appearance of soil changes above and below the water table due to a change in the oxidation state of iron. What is the change and why does it occur?
230. Why do salts accumulate at the surface in drier climates? Give examples of these salts.
231. What geological structures are necessary for an Artesian well?
232. Why does the age of groundwater change with depth?
233. What is the chemical structure of clay? Why is it plastic and 'greasy' when wet? (cf. Table 6.4)
234. What are the five main functional groups found in humic acid?

Exercises

235. Consider Figure 6.2. Which soil type can hold the most water and why? How does this property relate to the hydraulic conductivities of the soils shown in Table 6.3?
236. Draw the upper half of Figure 6.6 but write the names of the elements and their oxidation states. Identify the silicate and gibbsite regions.
237. Describe the 1:1 and 1:2 mineral structures and give examples of each.
238. Why is montmorillonite called water-expanded pyrophyllite? (Cf. Figures 6.10, 6.13a and 6.13b).
239. Consider Table 6.5. Why do humus and smectite have high cation exchange capacities, and gibbsite and hematite low? Why do histosols have high cation exchange capacities, while ultisols and oxisols have low values?
240. Soil acidity.
    a Why are Al^{3+} and Fe^{3+} acidic cations whereas K^+, Ca^{2+} and Fe^{2+} are not?
    b Describe the changes in soil cations upon acidification. What effect does this have on soil fertility?
241. Consider 50 kg of soil. How many bacteria, fungi, algae and protozoa does it contain using the lower estimates in Table 6.9?
242. In a spodosol, what is the source of acidity? What effect does acidity have on aluminium and iron oxides and clay particles? In contrast, why do silicates leach out of tropical soils?
243. Soil organic content changes with latitude. How does it change? Why does it change?
244. What is the difference between an aquitard and an aquifer? Give an example of each.
245. How is soil air different from the atmosphere, and how is soil water different from rainwater?
246. How do carboxylates, phenolates and amines stick to silicate surfaces in the soil?
247. Why is chlorite, Figure 6.12, called brucite expanded talc? Describe the structures.
248. Minerals, microorganisms, fungi, plants and animals all contribute to the soil solution. Give examples of chemical entities that come from each.
249. Why does the water in the central region of the clay vessel in Figure 6.14 rise?
250. Figure 6.16 shows that the surface charge of rutile goes from positive to negative as pH increases. What is the chemical species responsible for the surface charge? Draw a figure.

251. Consider Table 6.7. What is the chemical structure of the surface for hematite at pH 4 and 9? For quartz at pH 4 and 9?

Questions for *Chemistry and the Environment*

Chapter 6.1 Structure of the soil

Exercises

252. Consider Bernoulli's equation, eq. 2.88.

The speed of groundwater flowing in a sandy soil was found to be 10^{-6} m s^{-1}, which corresponds to 9 cm/d. The groundwater is 5 mM $Ca(HCO_3)_2$ with the density 1.00 g / ml. The acceleration of gravity is 9.81 m s^{-2}.

Calculate:

a the velocity head, h_u

b the osmotic head h_o relative to pure water

c the elevation head h_z for a height difference of 10 m.

Chapter 6.2 Physics of soil water

Exercises

253. Calculate the porosity of a sample of many spheres which are situated in
    - *a* a hexagonal closest packed structure
    - *b* a cubic closest packed structure = face centered array of spheres
    - *c* a cubic body centered array of spheres
    - *d* a primitive cubic array of spheres

    Hint. In *a* and *b* each sphere has 12 nearest neighbours, in *c* each has 8, and in *d*, 6.
254. Consider a pure substance (cf. p. 38) with the molar mass $M = 10^3$ g / mol and the mass density $\rho = 0.9$ g / ml. Assume that it consists of spherical molecules, packed with the porosity $\varphi_\mathrm{p} = 1/3$. Show that the diameter of the molecules is approximately 1.3 nm.
255. A dry sandy soil has the density $\rho_\mathrm{tot,\,s} = 1.50$ g / ml and a dry loamy soil has the density $\rho_\mathrm{tot,\,l} = 1.30$ g / ml.

    In both cases the density of the particles is $\rho_\mathrm{par} = 2.65$ g / ml.

    Calculate the porosity φ_p for the two cases.
256. A soil sample has the following properties: The mass fraction of water $\rho_\mathrm{w} = 0.110$. The density of water $\rho_\mathrm{w} = 1.00$ g / ml, of the particles $\rho_\mathrm{par} = 2.65$ g / ml, and the total density $\rho_\mathrm{tot} = 1.45$ g / ml. Calculate *a* the volume fraction of water, φ_w, and *b* the porosity of the soil, φ_p.
257. The density of the top soil of a plowed field is $\rho_\mathrm{tot} = 1.33$ g / ml and the volume fraction of water, $\varphi_\mathrm{w} = 0.15$. Calculate *a* the total mass per hectare and *b* the mass of water per hectare for the top soil.
258. A free aquifer of sandstone has the hydraulic conductivity $\mu_\mathrm{D} = 2$ m / d. It is assumed to be homogeneous with the porosity $\varphi_\mathrm{p} = 0.15$, cf. eq 6.3. In one area the water table falls 15 m over a distance of 5 km.

    Calculate:
    - *a* the overall speed of the water
    - *b* the time an impurity, moved by convection, will take to travel 5 km.
    - *c* the speed of the water in the pores

Questions for *Chemistry and the Environment*

Chapter 6.3 Chemistry of soils

Exercises

259. 5.0 g of a cation exchange resin with ammonium cations was treated using surplus of sodium chloride solution, which liberates all ammonium. 200 ml of 1.0 M sodium hydroxide was added to the solution of ammonium, and finally the surplus was back titrated using 5.0 ml of 1.0 M hydrochloric acid. Determine the capacity of the cation exchange resin.

260. A cation resin has a capacity of 2.6 mmol/g. What is the maximum amount of calcium ion that can be absorbed on 6.0 g of resin.

261. An illite has the composition $K_{1,0\text{-}1,5}Al_4[Si_{7,0\text{-}6,5}Al_{1,0\text{-}1,5}O_{20}](OH)_4$. Explain how the concept 'isomorphic substitution' would apply to such a chemical species.

262. An illite has the composition $K_{2-x}Al_4[Si_{6+x}Al_{2-x}O_{20}](OH)_4$. Explain how the concept 'isomorphic substitution' would apply to such a chemical species.

263. A bentonite clay deposit from Montmorillon, France, contained a pink montmorillonite with the composition

$$(Ca_{0.27}Na_{0.03}K_{0.01})(Al_{3.37}Mg_{0.73}Fe^{III}_{0.09})[Si_{7.81}Al_{0.19}O_{20}](OH)_4\cdot(H_2O)_{2.05}$$

Answer the following questions using this clay to illustrate.

a What is meant by isomorphous substitution?

b Which ions are in octahedral coordination?

c Which ions are in tetrahedral coordination?

d What is the maximum ion exchange capacity (per mol) of the montmorillonite?

264. This exercise considers the *E*-pH diagram of the system Fe(II/III)-H_2O-CO_2-H_2S, Figure 5.11, p. 207.

The mineral pyrite, FeS_2, can form in sediments deposited in anaerobic conditions in wetlands. In many areas wetlands have been drained for agricultural use, exposing the sediments to air, and the sediments take on a reddish color.

Pyrite is formed from hematite and sulfate present in sediment which has later become anaerobic.

a Write the reaction equations describing the formation of pyrite.

Before the marsh soil was drained the soil solution had (*E*, pH) = (–200 mV, 6.3). The topsoil contained $w(FeS_2) = 25$ ‰. The cation capacity was $b_{CEC} = 0.6$ mol/kg and the mole fraction of aprotic cations was $x_{aprot} = 0.7$, cf. eq 6.27; the acidic cation was H^+.

After drainage the solution has (*E*, pH) = (+200 mV, 6.3). The Fe-S-H_2O system has come to equilibrium and the hydrogen ions formed have replaced the aprotic cations.

b Calculate the amount of hydrogen ions per Mg dried soil that are not bound to the soil matrix.

There is a line representing pH ≈ 6.3 in the *E*-pH diagram.

c Write the corresponding reaction equation and describe how the equation of the line was calculated using the concentrations of Figure 5.11 and the following constants:

Solubility product of siderite	$L(\mathrm{FeCO_3}) = 10^{-10.7}\ \mathrm{M}^2$
Acidity constant for $\mathrm{H_2CO_3(aq) + CO_2(aq)}$	$K_{a1} = 10^{-6.3}\ \mathrm{M}$
Acidity constant for $\mathrm{HCO_3^-}$	$K_{a2} = 10^{-10.3}\ \mathrm{M}$

265. The upper horizons of many temperate soil profiles contain manganese originating from enzymes, in weathered organic material. When the conditions are acidic and reducing the element occurs as $\mathrm{Mn^{2+}}$ but when groundwater reaches the surface it is oxidized by atmospheric oxygen.

a Write the equation for the oxidation of Mn(II) to $\mathrm{MnO_2}$ (the mineral pyrolusite) by dioxygen. This reaction is denoted '1'.

b Calculate the affinity A_1 (= $-\Delta_r G_1°$) for this process using the following standard electrode potentials (at 25 °C):

$$2.\ \mathrm{MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)} \qquad E_2° = 1.21\ \mathrm{V}$$

$$3.\ \mathrm{O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)} \qquad E_3° = 1.23\ \mathrm{V}$$

c Calculate the equilibrium constant K_1 at 25 °C.

Mn(II) forms complexes, $[\mathrm{Mn(hum)^{2+}(aq)}]$, with soil organic material, humus. The constant of formation is assumed to be $[\mathrm{Mn(hum)^{2+}}]/([\mathrm{Mn^{2+}}][\mathrm{hum}]) = 10^5\ \mathrm{M}^{-1}$, and the concentration of ligand $10^{-4}\ \mathrm{M}$.

d Calculate the equilibrium constant *K* for the formation of pyrolusite,

$$\mathrm{2[Mn(hum)^{2+}(aq)] + O_2(g) + 2H_2O(l) \rightarrow 2MnO_2(s) + 2hum(aq) + 4H^+(aq)}$$

Consider an acidic soil with pH ≈ 5, and a basic one with pH ≈ 8.

e Use the data to calculate the concentration of $\mathrm{Mn(hum)^{2+}}$ at the two pH values assuming that the pressure of dioxygen is 0.2 bar and that the soil contains a surplus of pyrolusite.

f Plants obtain manganese as complexes of Mn(II) with humus as a ligand. Under what conditions should one expect manganese deficiency in soil - despite a high contcentration of manganese?

266. The composition of the clay mineral illite varies with location due to isomorphic substitution. The overall structure is that of a 2:1 mineral, cf. Figure 6.13. Two examples will be used in this exercise:

I $\mathrm{KAl_4[Si_7AlO_{20}](OH)_4}$ $\quad M_\mathrm{I} = 758.67\ \mathrm{g\,mol^{-1}}$
II $\mathrm{K_2Al_4[Si_6Al_2O_{20}](OH)_4}$ $\quad M_\mathrm{II} = 796.66\ \mathrm{g\,mol^{-1}}$

a1 Define isomorphic substitution.

a2 Write the coordination number of each type of Al and Si.

a3 Define the cation exchange capacity, b_CEC

b1 Calculate the expected value of $b_\mathrm{CEC,\,II}$ of illite II.

The experimental value for this quantity was $b_\mathrm{CEC,\,II} = 0.16\ \mathrm{mol\,kg^{-1}}$

b2 Explain the difference between the expected and the measured cation exchange capacity.

Illite may be formed by the weathering of orthoclase, $\mathrm{KAlSi_3O_8}$, when it is exposed to water and carbon dioxide; the products include metasilicic acid.

c1 Write the reaction equation for the formation of illite I.

Illite is further weathered by water and carbon dioxide to give products that include gibbsite, $Al(OH)_3$.

c2 Write the reaction equation for the weathering of illite I.

A heath soil is acidic. Its pH is typically 3-4 in the *O* and *A* horizon and 5-6 in the *C* horizon, cf. Table 6.1.

d Explain with words and reaction equations why the podsol (the *E* horizon) mainly consists of quartz whereas the hard pan (*B* horizon) mainly contains gibbsite that is quite often reddish.

267. 5 g of a cation exchange resin as an ammonium salt was treated with a surplus of sodium chloride solution such that all ammonium was released. 20 ml of 1 M sodium hydroxide was added to this solution and then back titrated using 5 ml of 1 M hydrochloric acid. Calculate the capacity of the resin.

268. In order to determine its cation exchange capacity a sample of 10.00 g of soil (dried at 60 °C) was shaken with 100.00 ml of 1.00 M NH_4Cl until equilibrium and filtered. The liquid part contained Mg^{2+}, Ca^{2+}, Al^{3+}, Na^+ and K^+. The solid part was placed in a column, washed with water and then with 0.5 M of KCl,

$$NH_4^+(\equiv R^-) + K^+ \rightarrow NH_4^+ + K^+(\equiv R^-)$$

Describe with words and reaction equations how $[NH_4^+]$ can be determined by a potentiometric titration of the eluate. Explain how the cation exchange capacity is calculated.

269. Continuation of problem 268: The original sample (10.00 g) contained 0.220 mmol Ca^{2+}, 0.080 mmol Mg^{2+}, 0.150 mmol K^+, 0.130 mmol Al^{3+}; the remaining part of the negative charge of the micelles was neutralized by H^+. The cation exchange capacity was $b_{cec} = 0.120$ mol / kg. 10.00 g of the dried soil sample was treated (to equilibrium) with 25.00 ml 0.010 M $CaCl_2$. Calculate pH of this solution.

270. Continuation of problem 269: The 'base saturation' is defined as the mole fraction

$$x_{\text{base satuation}} =$$

$$\{b(H^+) + 3\,b(Al^{3+})\} / \{b(H^+) + 3\,b(Al^{3+}) + b(Na^+) + b(K^+) + 2\,b(Mg^{2+}) + 2\,b(Ca^{2+})\}$$

cf. eq 6.27. Calculate the 'base saturation' of the soil sample described in problem 269.

Questions for *Chemistry and the Environment*

Chapter 7 Global cycles of the elements

Review

271. Explain the difference between the equilibrium between CO_2(g) and CO_2(aq) according to Henry's Law, and the general solubility of CO_2 in water. How does dissolved inorganic carbon (DIC) change with pH and temperature? (Cf. problem 194.)
272. Explain the role of deep water formation in removing CO_2 from the atmosphere.
273. Draw Figure 7.4 but add arrows for anthropogenic nitrogen fixation.
274. Thermodynamics says that the transformation of N_2 and O_2 from the atmosphere to make nitric acid dissolved in the ocean has a positive affinity. Why doesn't this happen?
275. What acid is consumed and produced in the synthesis of superphosphate fertilizer?
276. Using the data in Figure 7.8, what is the lifetime of Cl in the atmosphere? What fraction of Cl is found in the oceans?

Exercises

277. Draw a logarithmic axis extending from 10^{14} to 10^{22}. Place each of the species in Table 7.1 on the axis. Label the regions covered by the units Pg, Eg and Zg.
278. Consider Figure 7.2, the carbon cycle.
    - *a* What is the lifetime of C in each reservoir?
    - *b* Apply the mass balance equation, $\mathrm{d}m/\mathrm{d}t = r_{\mathrm{in}} - r_{\mathrm{out}}$ (mass flux), to the atmospheric reservoir. List the individual source and sink terms and sum to obtain the annual change in the mass of atmospheric carbon. Compare this derived value with the measured value, obtained by analyzing Figure 7.3.
    - *c* Make a graph over a 100 a timescale showing each of the four terms in eq 7.1 and the total.
    - *d* Estimate the size of the annual variation in the atmospheric mixing ratio of CO_2, and calculate the ratio of this to the total mixing ratio of CO_2. What is the cause of the annual variation?
279. Consider Drax, Europe's largest coal-fired power plant, footnote *c*, p. 122; p.255.
    - *a* Using the values in Table 8.9 and the plants consumption of 11 Tg/a of coal in 2005, what is the annual use of O_2?
    - *b* Drax produces 1 Tg/a of gypsum as part of its strategy to reduce SO_2 emissions. What is the reaction? Determine the equivalent mass of $CaCO_3$ to yield the required Ca.
    - *c* Why are SO_2 emissions an environmental concern?
280. Table 7.6 summarizes the sources of fixed nitrogen. What fraction of the total is anthropogenic (fertilizer and combustion)?
281. Compare the S and N cycles shown in Figures 7.7 and 7.4. What are the differences?
282. Write the reactions by which Mo could be extracted from low grade ore using bacterial leaching (in analogy to reactions, eqs 7.40 to 7.44). What is the current market value of Mo?
283. Explain the oceanic 'biological pump' that removes CO_2 from the atmosphere.
284. Eq 7.4 would seem to counteract the net production of CO_2 through the production of cement,

eq 7.2. Nonetheless, cement manufacture emits 440 Tg of CO_2 to the atmosphere each year. How can this be?

285. Read the value of the equilibrium constant in Figure 7.5 for a temperature of 1000 °C. What would the equilibrium partial pressure of NO be in an atmosphere heated to 1000 °C at 1 bar pressure?
286. What is the dominant ionic form of phosphate in the ocean (consider pK_a's and the ocean's pH)?
287. Name the main species emitted to the atmosphere that yield acid rain. What reactions convert these species to acids? How can acid rain be minimized?
288. Name one element that is mainly found in the atmosphere, one mainly found in the hydrosphere, and one mainly found in the lithosphere.
289. Write characteristic examples of *a* oxidative and *b* reductive nitrogen fixation.
290. Show by examples and using balanced reaction equations that nitric acid is an oxidizing acid.
291. Oxidation of hydrogen sulfide in the atmosphere may give two products. Write the reaction equations and specify name, color and state of aggregation (25 °C, 1 bar) for the products.
292. Write formulas for eight sulfur containing species that occur in Nature; the examples must include at least five different oxidation states of sulfur.
293. Write a balanced reaction equation for the natural process where hydrogen sulfide is oxidized to sulfuric acid.

Questions for *Chemistry and the Environment*

Chapter 7.3 Nitrogen

Exercises

294. *Note.* This problem uses the units hectare, ha = $10^4\,\mathrm{m}^2$, and year, a = 3.1557×10^7 s.

A report has described the runoff water from 20 km^2 tilled fields in Denmark. The average yearly values of salts in this water, measured during 10 a, are given below. Rainfall was 360 $\mathrm{mm\,a^{-1}}$ of which 120 $\mathrm{mm\,a^{-1}}$ was registered as drainage water.

dihydrogenphosphate	37.0 $\mathrm{g\,ha^{-1}\,a^{-1}}$
nitrate	21.91 $\mathrm{kg\,ha^{-1}\,a^{-1}}$
ammonium	63.0 $\mathrm{g\,ha^{-1}\,a^{-1}}$
potassium ion	1.03 $\mathrm{kg\,ha^{-1}\,a^{-1}}$

a1 Suppose that additional ions not included in the list are hydrogen or hydroxide. Calculate the average value of pH in the riverwater.

a2 Discuss the applicability of this method of pH determination.

The fields were supplied with 200 $\mathrm{kg\,ha^{-1}\,a^{-1}}$ of nitrate fertilizer. The mass fractions were 70 % ammonia and 30 % ammonium nitrate.

b Calculate the ratio between the amounts of nitrogen(V) and nitrogen(–III) in the fertilizer and the drainage water, respectively.

c Explain (words and reaction equations) why the two ratios are different.

Questions for *Chemistry and the Environment*

Chapter 7.5 Sulfur

Exercises

295. Deposition of airborne sulfuric acid in Denmark is estimated to be 20 kg $\mathrm{ha^{-1}}$ per year of elemental sulfur, S. Its origin is sulfur in fuel. Write relevant reaction equations and calculate the amount flux density using the units: $\mathrm{mmol\,a^{-1}\,m^{-2}}$ and $\mathrm{kg\,a^{-1}}$ hectare .
296. In Denmark the soil often contains chalk (calcium carbonate) which reacts with sulfuric acid from the atmosphere forming calcium hydrogencarbonate. Write the balanced reaction equation and show that 20 kg of S in form of sulfuric acid may wash out 125 kg of chalk.

Questions for *Chemistry and the Environment*

Chapter 8 The Chemicals Industry

Review

297. Give three examples of industrial reductions, and three examples of industrial oxidations.
298. Name four common industrial bases.
299. Which industrial oxidant has the highest production, and how is it produced and purified?
300. What are the most important industrial reducing agents and how are they produced?
301. Nitrogen, potassium and phosphorus are used in agriculture to maintain soil fertility. Why are these elements lost from soil?
302. How many of the top 20 industrial chemicals by production are inorganic?
303. How is the synthesis of polyamides similar to that of polyesters?
304. What raw materials are used to make Portland cement?
305. Why does cement production result in the emission of CO_2 to the atmosphere?
306. Give three examples of how cement production can be used to recycle materials.
307. How is NO_x emission from cement production reduced?
308. What metals can be released into the environment by cement production?
309. What is the red mud generated by aluminum production?
310. Why is lignin removed from pulp when making paper? What can be done with the lignin?
311. What is the environmental danger of using Cl_2 to bleach paper, and how can this be avoided?
312. Why is the industrial production of chlorine linked to the production of sodium hydroxide?
313. Why has the Leblanc process been replaced by the Solvay process?
314. What is the leading use of industrial chlorine?
315. What is PVC used for?

Exercises

316. What was the per capita worldwide consumption of energy in 2008 using energy units of oil equivalent? What fraction of global energy consumption in 2008 was renewable? Non-fossil?
317. Consider the phase diagram for iron-carbon alloys, Figure 8.3. What is pig iron and why does it have 4.3 % C?
318. Which of the commodities in Table 8.1 are polymers? Which have productions that have more than doubled from 1994 to 2007?
319. Consider a power plant that burns 30 Gg of bituminous coal per day. Given the composition found in Table 8.9, what amount of sulfur is oxidized per day? 90 % of the SO_2 produced is trapped and converted to gypsum using a limestone slurry. Write the reaction involved. What mass of gypsum is produced per day?
320. Write the reaction forming polyester from ethylene glycol and terephthalic acid.
321. What is the difference between starch and cellulose?
322. Consider eq 8.8 representing the production of iron from ore. What is the change in oxidation state of Fe and C? Why is limestone added to this process?
323. Why should the ratio of CO to CO_2 be greater than 6.3 in a blast furnace?

324. What is shown by the Ellingham diagram Figure 8.4? Using this diagram, which metal oxide ores can be refined by direct reduction using C? Why can't CaO be reduced in this way? How can Al_2O_3 and TiO_2 be refined?

Questions for *Chemistry and the Environment*

Chapter 8.1c Fertilizers

Exercises

325. Calculate the mole fraction and the mass fraction of nitrogen in ammonium sulfate, ammonium nitrate, urea and ammonia (liquid and gas).
326. Explain through a reaction equation whether ammonia in water is an acid or a base.
327. Show through a balanced reaction equation that the natural microbial oxidation of ammonia yields an acid.
328. The phosphate fertilizer 'super phosphate' is produced by treating hydroxylapatite, $Ca_5(OH)(PO4)_3$, with concentrated sulfuric acid in the (amount of substance) ratio $n_{Ca} : n_{H_2SO_4} = 10{:}7$, where n_{Ca} refers to the amount of calcium in apatite. Write the balanced reaction scheme.
329. Fertilizer contains the elements nitrogen, phosphorus and potassium (but not as free elements!). The content is often given as the mass fractions (in %): $w(N)$-$w(P_2O_5)$-$w(K_2O)$, in so-called NPK-fertilizer.

     a Calculate the mass fractions $w(N)$, $w(P)$ and $w(K)$ in a 25-3-6 fertilizer.

     Calculate $w(N)$-$w(P_2O_5)$-$w(K_2O)$ for the following fertilizers:

     b urea

     c diammonium hydrogen phosphate

     d a mixture specified by $w(\text{cyanamide})/w(\text{potassium nitrate}) = 0.5$.
330. The most common nitrogen fertilizers are ammonium sulfate, ammonium nitrate, urea, cyanamide, liquid ammonia and calcium nitrate nonahydrate.[1]

     a Calculate the mass fraction of nitrogen for each species.

     b Write balanced reaction equations for the industrial preparation of each species.

     c Write reaction equations for possible microbial processes.

     d Let $p_u = val/m_u$ be the price per mass of urea (= value / mass) and similarly $p_c = val/m_c$ the price per mass of calcium nitrate nonahydrate. At what value of the ratio between the price per kg of the two fertilizers, p_u/p_c, is the production of one or the other economically favorable?
331. Fluorapatite is $Ca_5(F)(PO_4)_3$. Write the balanced reaction equations for the preparation of *a* superphosphate and *b* phosphoric acid from fluorapatite.

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[1] $Ca(NO_3)_2 \cdot 9H_2O$, previously called calcium nitrate enneahydrate.

Questions for *Chemistry and the Environment*

Chapter 8.2 Heavy industry

Exercises

332. An iron ore with a suitable amount of hematite, Fe_2O_3, is to be reduced with coke, C, in a blast furnace. The temperature at the bottom of the furnace is $t \approx 2000$ °C and at the top $t \approx 200$ °C, cf. Figure 8.1. The reaction $CO_2 + C \rightleftarrows 2CO$ is endothermic and has the equilibrium constant $K_p \approx 1$ bar at $t \approx 900$ °C, cf. Figure 8.4. Write a balanced reaction equation for the reduction of iron(III)oxide with carbon at *a*: $t \approx 1600$ °C and *b*: $t \approx 600$ °C, respectively.

Questions for *Chemistry and the Environment*

Chapter 9 Environmental impact of selected chemicals

Review

333. Early insecticides included lead arsenate, cryolite, fluorosilicates and ligroin. Write the chemical formula of each and explain their toxicity.
334. In general, is a lipophilic species hydrophilic or hydrophobic?
335. Describe how pheromones can be used as an alternative to insecticides. Why is this an example of green chemistry?
336. Draw a possible structure for atrazine on a phylosillicate surface.
337. What is a congener? Give an example.
338. What is the difference between a soap and a detergent?
339. Which man-made chemicals have the potential to be Persistant Organic Pollutants?
340. What qualities reduce the environmental impact of a pesticide?

Exercises

341. Consider eqs 9.1 and 9.2. Write the structure of the gem diol and the mechanism of its conversion to DDT. Why does this synthesis produce a mixture of products? Give three examples of possible products other than p,p'-DDT.
342. What is the difference between C_3 and C_4 photosynthesis? Give examples of three C_3 and three C_4 crops. Explain why some herbicides are only used to protect C_4 plants.
343. Consider the environmental accident in Hungary in October 2010 in which 1 Mm^3 of 'red mud' from aluminium manufacture escaped from the containment pond. Bauxite, the ore refined to generate aluminium, contains 30 to 54 % alumina, Al_2O_3. The rest is a combination of silica, iron oxides and titanium dioxide. In the Bayer process, bauxite is digested using a solution of NaOH at 175 °C. This converts alumina in the bauxite into tetrahydroxy aluminate. The liquid is taken away and dehydrated converting the complex back to alumina. In the final step molten aluminium oxide (with the addition of cryolite, Na_3AlF_6, a 'flux' that decreases the melting point) is electrolyzed to yield aluminium metal, cf. p. 292.

     Write the reaction equations for the processes above. Explain where 'red mud' comes from. Why is it red and caustic?
344. Glyphosate is drawn in eq 9.13 and the pK_a values are given in the text, p. 318. Draw the speciation diagram and label the species present in the diagram. What is the main chemical form of glyphosate given a soil pH of 6.2?
345. The octanol-water partitioning constant for TCDD (cf. eq 9.23) is $K_c^{ow} = 10^{6.8}$, and in fact most insecticides tend to be hydrophobic. Why is this, and what consequence does it have for the fate of stable insectides in the food chain?
346. Dioxins have a high melting point, a high boiling point, low reactivity and a low vapor pressure. Yet, they have been detected everywhere on the surface of the earth. How is this possible? Give an example of a dioxin.
347. What is the difference between bioaccumulation and biomagnification? Why do lipophilic

compounds tend to bioaccumulate?

348. How are the structures of dieldrin and endosulfane related to aldrin? Draw the structure of endosulfane's hydrolysis to give SO_2 and a diol.

349. How does the cation exchange capacity of humus (Table 6.6) compare with the cation exchange capacity of ion exchange resin (cf. text above eq 9.67)? Assume the density of humus is 1 g/ml.

350. Why is it better for the environment to only synthesize one enantiomer of a pesticide? Give an example.

351. What are the physical characteristics of persistent organic pollutants? Where are they found and how do they get there?

352. Some synthetic detergents contain 25 % to 45 % sodiumtriphosphate (sodium tripolyphosphate). Its most important role is to soften hard water by forming a 1:1 complex between the triphosphate anion 'L' and magnesium and calcium ions. The equilibrium constants are $K(\mathrm{NaL}) = 10^{2.8}\,\mathrm{M}^{-1}$, $K(\mathrm{MgL}) = 10^{8.6}\,\mathrm{M}^{-1}$ and $K(\mathrm{CaL}) = 10^{8.1}\,\mathrm{M}^{-1}$. Write the reaction equations connected to the equilibrium constants. Why is phosphate a problem for the environment?

353. What is the significance of the octanol-water partitioning coefficient for the environmental impact of man-made chemicals?

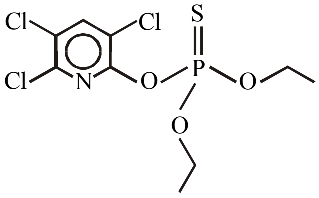
354. Calculate the ratio of the mass of red mud to aluminium metal when refining bauxite with an alumina content of 40 % by weight. Assume that half of the mass of the red mud is water. Why is the red mud an environmental hazard? Why is it red?

Questions for *Chemistry and the Environment*

Chapter 9.1 Pesticides

Exercises

355. Consider chlorpyrifos: *O*,*O*-diethyl *O*-3,5,6-trichloropyridin-2-yl phosphorothioate, $C_9H_{11}O_3NPSCl_3$,



$M = 350.59$ g/mol

Chlorpyrifos is the IUPAC/ISO name of a pesticide introduced in 1965 with the trade name Dursban. It has been used as an insecticide, in particular in the USA (coffee, cotton, maize; *ca.* 1 kg/ha) and in South America (bananas). In the late 20th century, consumption in the USA for indoor use (termites, ants, cockroaches) was *ca.* 10 Gg/a.[2] Its potency is due to the primary product of hydrolysis, *O*,*O*-diethyl thiophosphate, which is further hydrolyzed by enzymatic processes into *O*,*O*-dithyl phosphate which inhibits the enzyme cholinesterase that regulates signal transmission in nerves.

Oxidation of chlorpyrifos gives rise to a chemical oxygen demand which can be determined by a titration with dichromate, cf. p. 121; here the elements N, P and Cl do not change oxidation number.

a1 Calculate w_{COD}.

Excessive use of chlorpyrifos in banana plantations of Costa Rica was detected in the rivers. The observed the mass fraction of chlorpyrifos was 19×10^{-6}.

a2 Calculate the chemical oxygen demand w'_{COD} of river water due to this pollution.

The biological oxygen demand w_{BOD} may be calculated by also considering the oxidation of nitrogen (to nitrate).

b1 Calculate the biological oxygen demand w_{BOD}.

b2 Give a short account of how this quantity is determined experimentally.

The lifetime of chlorpyrifos in the upper layers of the soil is 2-4 months; it decays by hydrolysis of the esters and later of the thiophosphate.

c Write the reaction equations for pH 6.

The product 3,5,6-trichloropyridin-2-ol (trichloropyridinol) is broken down slowly and it may therefore be transported far from its source. Trichloropyridinol, HA, is a base whose conjugate acid H_2A^+ has the acidity exponent $\mathrm{p}K_{\mathrm{H_2A^+}} = 6.7$. Trichloropyridinol also enters a tautomeric equilibrium:

---

[2] Note: ha = hectare = 10^4 m^2, not 'hecto year'; a = year.

trichloropyridinol ⇄ trichloropyridone $K = c_{\text{trichloropyridone}} / c_{\text{trichloropyridinol}} \approx 2\times10^{-3}$

and this mixture, HA', is an acid with the acidity exponent $pK_{HA'} = 10.8$, the conjugate base being trichloropyridinolate, A^-.

d1 Draw the speciation diagram as function of pH, cf. the footnote *a* on p. 182.

d2 Calculate the isoelectric point, pH_{iep}.

This solution may be titrated using strong acid.

e1 Calculate the alkalinity of 0.01 M sodium trichloropyridinolate in water.

e2 Calculate the pH of this solution.

e3 Calculate the pH at the normal endpoint of the titration.

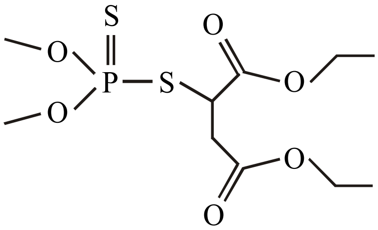
f1 Make a sketch of the alkalinity *A* as a function of pH during the titration, and continue beyond the end point to illustrate what happens at low pH.

f2 Make a sketch of the variation of the buffer value *β* for the same range of pH.

g1 Write in detail the definition of $K_{HA'}$.

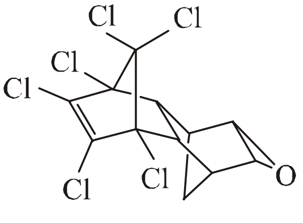
g2 Assess the importance of the tautomeric equilibrium on the acid-base equilibrium and on other relevant conditions.

356. This exercise considers the chemistry of two insecticides,



Malathion; $C_{10}H_{19}O_6PS_2$; $M = 330,35$ g/mol.

Malathion is used against boll weevils, locusts and malaria mosquitoes.



Dieldrin; $C_{12}H_8Cl_6O$; $M = 380,91$ g/mol.

Dieldrin has been banned since 2004. Production is believed to have ceased overall.

A warehouse containing pesticides close to Hargeisa, Somalia, was bombed in May 1988. Following the incident, residents emptied the unharmed containers onto the ground. The warehouse contained malathion and dieldrin. The area was investigated by chemists and biologists in March 1993. At that time the upper horizons of the soil in an area of 3700 m^2 around the site were contaminated by dieldrin, 5.18 kg m^{-3}, but malathion could not be detected. Even five years after the release of these pesticides into the environment, frogs and lizards died a few hours after they had been in contact with the contaminated soil.

The chemical oxygen demand, w_{COD}(m), of malathion may be determined by dichromate titration, cf. p. 121.

a1 Calculate w_{COD}(m).

The chemical oxygen demand of dieldrin is $w_{COD}(d) = 1.008$.

a2 Calculate the biological oxygen demand, w_{BOD}(d), of water containing 5 mg / l of dieldrin.

Malathion is sparingly soluble in water but it is subject to hydrolysis, which is rapid in basic solution. Hydrolysis in acidic solution yields the products methanol, ethanol, hydrogen sulfide, phosphoric acid and thiomalic acid (the same as mercaptobutanedioic acid, $HO_2C{\cdot}CH_2{\cdot}CHSH{\cdot}CO_2H$).

b1 Write the reaction equation for the hydrolysis of malathion at pH ≈ 7.8.

Suppose that 0.1 M of malathion was hydrolyzed at pH ≈ 7.8.

b2 Calculate the alkalinity *A* of the final solution.

A 0.1 M solution of disodium thiomalate, $NaO_2C{\cdot}CH_2{\cdot}CHSH{\cdot}CO_2Na$, is titrated with strong acid.

c1 Calculate the pH and alkalinity before titration.

c2 Calculate the alkalinity at three characteristic pH-values.

c3 Make a sketch of the speciation diagram and the buffer value as a function of pH in the pH-interval $13 > pH > 1$.

Tropical soils contain the mineral goethite, FeO(OH).

d Discuss and comment on whether phosphate species from the hydrolysis *b1* can be transported by groundwater.

Five years after the spill the mass of eldrin per mass of topsoil was 0.50 mg / kg 350 m from the site and 0.05 mg / kg at a distance of 9 km.

e1 Calculate the gradient of concentration.

Biological investigations showed that 3 km from the site no chloroalkanes could be detected in the food chain.

e2 Name two conditions necessary to conclude anything about the pollution of dieldrin at this distance.

Acidity exponents:

phosphoric acid, H_3PO_4 $pK_1 = 1.72$ $pK_2 = 5.72$ $pK_3 = 11.74$

hydrogen sulfide, H_2S $pK_1 = 6.83$ $pK_2 = 14$

thiomalic acid,

$HO_2C{\cdot}CH_2{\cdot}CHSH{\cdot}CO_2H$ $pK_1 = 3.2$ $pK_2 = 4.60$ $pK_3 = 10.45$

Equilibrium constants (H_3L = thiomalic acid)

$Fe^{3+} + H_3L \rightarrow FeHL^+ + 2H^+$ $K_a = 2.57$ M

$Fe^{3+} + H_2PO_4^- \rightarrow FeH_2PO_4^{2+}$ $K_b = 10^{3.47}\,\mathrm{M}^{-1}$

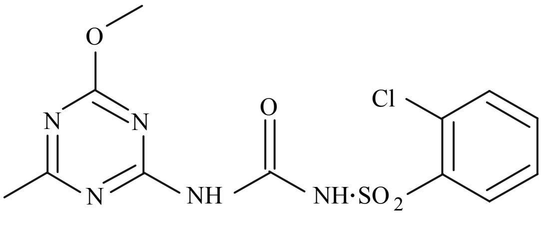
$Fe^{3+} + HPO_4^{2-} \rightarrow FeHPO_4^+$ $K_c = 10^{8.30}\,\mathrm{M}^{-1}$

$Fe^{3+} + PO_4^{3-} \rightarrow FePO_4{\cdot}2H_2O(s)$ $K_d = 10^{26.4}\,\mathrm{M}^{-2}$

$Fe^{3+} + 3HO^- \rightarrow FeO(OH)(s) + H_2O$ $K_e = 10^{41.5}\,\mathrm{M}^{-4}$ (goethit)

$H^+ + HO^- \rightarrow H_2O(l)$ $K_w = 10^{14.0}\,\mathrm{M}^{-2}$

357. Environmental chemistry of chlorsulfuron.



Chlorsulfuron. $C_{12}H_{12}ClN_5O_4S$; $M = 357.8\ \mathrm{g/mol}$
Systematic names in general use:
1-(2-chlorophenyl)sulfonyl-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea (IUPAC)
2-chloro-*N*-[(4-methoxy-6-methyl-1,3,5-triazin-2 yl)aminocarbonyl]benzene sulfonamide (CAS)

The sulfonylurea herbicide chlorsulfuron is a 3rd generation herbicide which was developed in the 1970s. It blocks the biosynthesis of the amino acids valine and isoleucine in plants and is therefore lethal to dicots; it is widely used in part because the dosage is only 4 g per hectare. The environmental chemistry of chlorsulfuron is discussed here; relevant acidity and basicity exponents are given at the bottom of this problem.

The chemical oxygen demand of chlorsulfuron w_{COD} may be determined by oxidation using basic permanganate. Here chlorsulfuron (→ C^{IV}, S^{VI}, N^{-III}, Cl^{-I}) is boiled with potassium permanganate (→ MnO_2) and the solution is kept basic using sodium carbonate.

a Calculate w_{COD}.

When chlorsulfuron is oxidized biological nitrogen is also oxidized (→ N^V).

b Calculate the biological oxygen demand, w_{BOD}.

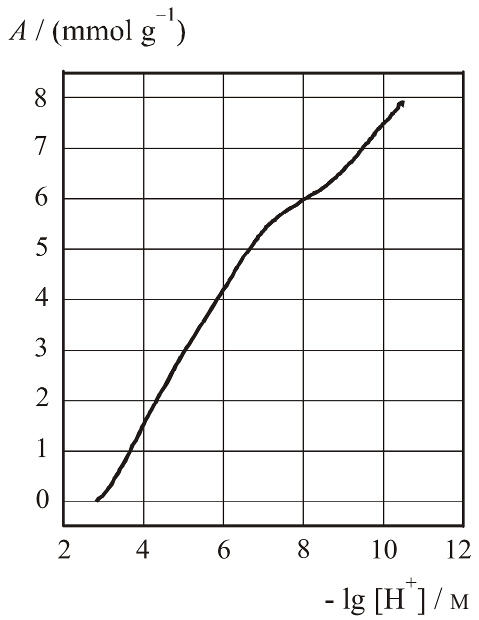
Basic hydrolysis of chlorsulfuron for a short time yields 2-chloro-benzenesulfonate, urea and 4-methoxy-6-methyl-1,3,5-triazine-2-olate. In this example 0.50 mmol chlorsulfuron is treated for a short time in 100 ml 0.0400 M sodium hydroxide.

c1 Calculate the alkalinity *A* of the final solution.

Basic hydrolysis of chlorsulfuron for a longer time yields 2-chloro-benzenesulfonate, ammonia, carbonate and 4-methoxy-6-methyl-1,3,5-triazine-2-olate. 0.50 mmol chlorsulfuron is treated for a longer time in 100 ml 0.0400 M sodium hydroxide.

c2 Calculate the alkalinity *A* of the final solution.

Consider the alkalinity of a spodosol fulvic acid (cf. Figure 6.17):



In the Figure the alkalinity A of a fulvic acid (mass density $\rho = 0.5$ g ml^{-1}) is drawn as a function of pH. The fulvic acid is known to contain the following functional groups: carboxylic acids, phenols, ketones, ethers and anisoles.

d What conclusions can be drawn from the figure and the data provided?

Assume that hydrolysis *c2* takes place in a field at pH 7.

e1 Write the reaction equation.

e2 Which species are retained in the fulvic acid?

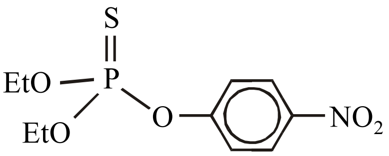
e3 Discuss the mechanisms by which these species are retained.

pK_a values	
2-chlorobenzenesulfonic acid	≈ –3
4-methoxy-6-methyl-1,3,5-triazine-2-ol	≈ 11
ammonium	≈ 9.3
carbonic acid (aq)	≈ 6.5
hydrogencarbonate	≈ 10.5
pK_b value	
urea	≈ 14

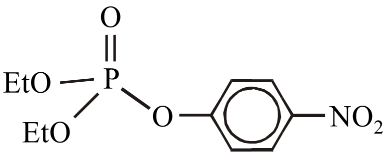
358. An introduction to the chemistry of fonofos.

Background. While the insecticide parathion, species **A**, is a very efficient insecticide it is poisonous to mammals. Its toxicity arises because the enzyme MFO (mixed function oxidase) catalyzes the conversion of **A** to paraoxon, species **B**, which inhibits the enzyme cholinesterase. Parathion has been phased out everywhere.

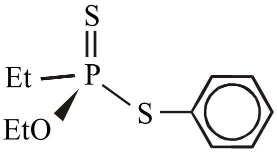
A new more specific insecticide, fonofos, was created with the goal of targeting insects while reducing unwanted effects on mammals. Fonofos is the optically active derivative of the phosphonic acid shown as species **C**. This species is 6 to 10 times more potent than its enantiomer. As for fonofos, its potency is due to the formation of the corresponding oxon, species **D**. Species **E** was created for the present problem.



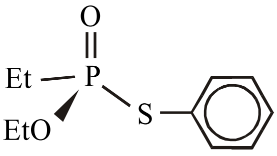
A *Parathion*, *O*,*O*-diethyl *O*-(4-nitrophenyl)phosphorothioate



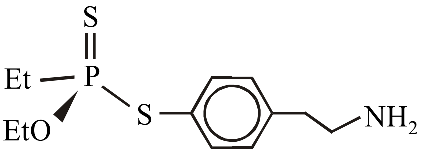
B *Paraoxon*, diethyl 4-nitrophenyl phosphate



C *Fonofos*, (*S*)-*O*-ethyl *S*-phenyl ethylphosphonodithioate
$C_{10}H_{15}OS_2P$; $M = 246.32$ g/mol



D *Fonooxon*, (*R*)-*O*-ethyl *S*-phenyl ethylphosphonothioate



E (*R*)-*O*-ethyl *S*-[4-(2-amino ethyl)phenyl] ethylphosphonodithioate

The chemical oxygen demand, w_{COD}, of fonofos may be determined by dichromate titration, cf. p. 121.

a1 Calculate w_{COD}.

a2 Calculate w_{COD} of a sample of water containing 1.5 mg m^{-3} fonofos.

The biological oxygen demand may be calculated on the basis of a metabolic process where the oxidation does not include ethylphosphonic acid, $C_2H_5P(O)(OH)_2$, and thiophenol.

b Write the reaction equation and calculate w_{BOD}.

When fonofos is hydrolyzed at pH 9 the products include derivatives of hydrogen sulfide, ethanol, ethylphosphonic acid and thiophenol.

c1 Write the complete reaction equation.

c2 Assume that 25 mg dm^{-3} of fonofos is hydrolyzed at room temperature; calculate the pH, alkalinity and buffer value.

The hydrolysis of fonofos is a slow reaction allowing the compound to spread into groundwater. Consider compound **E**, designed to prevent this.

d Explain how **E** may be retained in a farm soil.

Hint: Discuss adsorption on clay minerals and humus.

1 mmol 4-(2-aminoethyl)benzenethiol is dissolved in 100 ml 0.05 M sodium hydroxide.

e Write the reaction equation and calculate the alkalinity of the resulting solution.

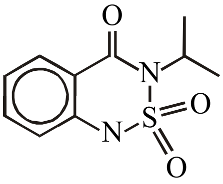
This solution may be titrated with strong acid.

f Draw the variation of the alkalinity and the buffer value as a function of pH; calculate four characteristic pH values.

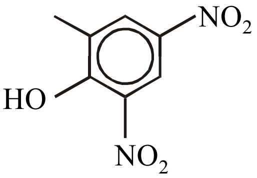
Acidity exponents at 25 °C:

ethylphosphonic acid	$pK_1 = 2.28$	$pK_2 = 7.79$
hydrogen sulfide	$pK_1 = 6.83$	$pK_2 \sim 14$
thiophenol	$pK = 7.59$	
2-phenylethylammonium	$pK = 9.92$	

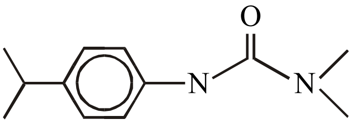
359. The exercise considers the fate of some general herbicides in farm soil.
The compounds **A** - **G** are herbicides; **H** is produced in the degradation of **G**.



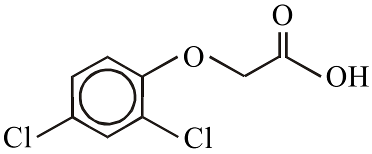
A *bentazone*, 3-isopropyl-1*H*-2,1,3-benzothiadiazin-4(3*H*)-one 2,2-dioxide



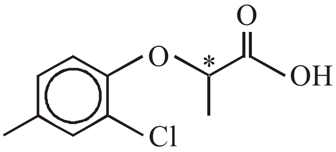
B *DNOC*, 2-methyl-4,6-dinitrophenol (2,4-dinitro-orthocresol)



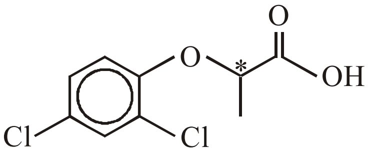
C *isoproturon*, 3-(4-isopropylphenyl)-1,1-dimethylurea



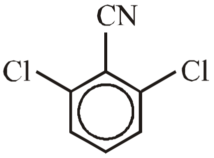
D *2,4-D*, 2,4-dichlorophenoxyacetic acid



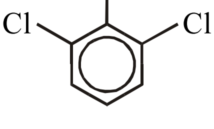
E *mechlorprop-P*, (*R*)-2-(4-chloro-2-methylphenoxy)propanoic acid



F *dichlorprop-P*, (*R*)-2-(2,4-dichlorophenoxy)propanoic acid



G *dichlobenil*, 2,6-dichlorobenzonitrile



H *BAM*, 2,6-dichlorobenzamide

The compounds **A - G** are general use herbicides, although some (*e.g.* bentazone and dichlobenil) have been banned within the past 15 years. Nevertheless, contamination by BAM, a degradation product of dichlorobenil, is a common reason for decommissioning water treatment plants in Denmark.

DNOC and isoproturon are retained in soils whereas bentazon, the phenoxy acids and BAM are not. Generally, these herbicides are broken down within 80 days whereas decomposition of BAM requires much more time.

Some properties of the componds are given in the following table.

1	*2*	*3*	*4*	*5*	*6*
A	bentazone	$C_{10}H_{12}N_2O_3S$	240.28		
B	DNOC			$pK_a = 4.4$	
C	isoproturon	$C_{12}H_{18}N_2O$	206.29		2.294
D	2,4-D	$C_8H_6Cl_2O_3$	221.04	$pK_a = 3.0$	1.086
E	mechlorprop-P	(R)-$C_{10}H_{11}ClO_3$	214.65	$pK_a = 3.2$	1.640
F	dichlorprop-P	(R)-$C_9H_8Cl_2O_3$	235.07	$pK_a = 3.0$	1.225
G	dichlobenil	$C_7H_3Cl_2N$	187.99		
H	BAM	$C_7H_5Cl_2NO$	190.03		1.095

1. The bold lettters refer to the formulas above.
2. Non-systematic names.
3. Stoichiometric formulas.
4. Molar mass, $M / \mathrm{g\,mol^{-1}}$
5. Acidity exponent, pK_a, at ambient temperature.
6. Chemical oxygen demand, w_{COD}, as determined by a dichromate titration. In this method the elements Cl, N and O are not oxidized.

a Fill in columns *3* and *4* and calculate w_{COD} for compounds **A** and **B**.

b Calculate w_{COD} of aqueous solutions containing $800\,\mu\mathrm{g\,l^{-1}}$ of each of the compounds **A** to **F**.

c Estimate the pH of solution *b*.

d Estimate the buffer value of a solution containing $800\,\mu\mathrm{g\,l^{-1}}$ of 2,4-D at pH 5.

e Soils commonly contain clay minerals and humus. Explain why isoproturon is retained in this soil whereas BAM is not.

Chapter 9.6 Water treatment

Exercises

360. Alum, $KAl(SO_4)_2 \cdot 12H_2O$, is a crystalline species that is easily dissolved in water; this acidic solution contains hexaaquaaluminium(3+). Water, contaminated with humus, may be purified by the addition of alum. Write the relevant reaction equations.
$\mathrm{p}K\{Al(aq)_6^{3+}\} = 4.3$; $\mathrm{p}K\{H_2CO_3{+}CO_2\} = 6.5$; $\mathrm{p}K\{HCO_3^-\} = 10.3$.

361. A person equivalent (PE) is a quantification of the environmental impact of a human being. In the present context we consider only the amount of wastewater received by a wastewater treatment plant, on average, $q_{\mathrm{PE}} = 200$ kg/d.
The lifetime of wastewater in a root zone plant must be at least $\tau = 15$ d. Calculate the minimum size of a plant with a capacity of $300\, q_{\mathrm{PE}}$.

362. An industrial wastewater has the concentration of sulfuric acid $c(H_2SO_4) = 5$ mM. This water must be diluted to pH = 4.3 with fresh water before it can be discharged to a treatment plant. The fresh water has pH 6.5 and alkalinity 2×10^{-3} M. Calculate the (volume) mixing ratio necessary to give the required dilution.

Questions for *Chemistry and the Environment*

Chapter 10 The Chemistry of Climate Change

Review

363. Define: Albedo, climate sensitivity parameter, radiative forcing, global warming potential, greenhouse gas.
364. What is a climate feedback? Give three examples.
365. What factors can cause long-term climate change?
366. Name some natural emissions that affect climate.
367. Why isn't the annual peak insolation at the north pole equal to the annual peak insolation at the south pole?
368. Explain the role of the ice-albedo feedback in amplifying the Milankovitch cycles.
369. What is the definition of climate? What methods have been used to determine what the climate was before thermometers were invented?
370. What is the equivalent CO_2 concentration reduction achieved by the ban on CFC gases? Use the CFC peak concentration Section 10.3a and the CFC-11 GWP given in Table 10.5. Assume that CFC-11 is 1/3 of all CFCs.

Exercises

371. Use eq 10.17 to calculate the solar constants for Venus and Mars. The orbital radii can be found in Table 1.3. How do you explain the surface temperatures seen on the three terrestrial planets?
372. Climate sensitivity parameter.
    - *a* Define the climate sensitivity parameter.
    - *b* The climate sensitivity parameter can be estimated using the simple radiative balance model. How much does the predicted surface temperature change if the blackbody radiant excitance of eq 10.19 is increased by 1 %? Derive the climate sensitivity parameter using this change.
    - *c* Assume that the climate changes in the Vostok record (Figure 10.6) are due to changes in CO_2. Estimate the change in temperature per change in CO_2 mixing ratio from the data shown in the Figure. Next, use Table 10.3 to calculate the change in CO_2 mixing ratio per change in radiative forcing. Finally, combine these two values to provide a separate estimate of the climate sensitivity parameter.
    - *d* Estimate the climate sensitivity parameter using the total net anthropogenic change in radiative forcing in Table 10.4 and the observed change in temperature in Figure 10.8.
    - *e* Discuss some factors that make the climate sensitivity parameter difficult to estimate.
373. Geoengineering has been proposed as a 'last chance' solution.
    - *a* Land use change (*e.g.* forest to field) has changed the absorptivity of the surface. How much change would be necessary to counteract a 1 °C temperature increase? Use eq 10.20.
    - *b* What change in albedo would be needed to counteract a 1 °C temperature increase? Use eq 10.21. How could this be done?
    - *c* The eruption of Mount Pinatubo in 1991 injected 1 Tg of SO_2 into the stratosphere, which cooled the global climate by 0.5 K for about a year (see dip in temperature in Figure 10.8).

Some have proposed that the planetary albedo and climate could be actively managed using missiles loaded with sulfur to enhance the stratospheric sulphate areosol layer. What mass of sulfur per year would be required to cool the climate by 1 °C? What would happen to the sulfur (photochemically) after the shells exploded? How long would the sulfur stay in the stratosphere?

374. Compare the emission spectrum of Earth (Figure 10.1) with the absorption spectra of the greenhouse gases shown in Figure 10.2. At what wavelength(s) can earthshine escape to space without being absorbed by atmospheric gases?
375. Looking at Table 10.1, it does not appear that burning fossil fuel by itself would yield enough energy to change the surface temperature. However, consider that energy use is confined to cities. Cities cover 3 % of the land which makes up 30 % of the surface. Compare fossil energy use with the energy of sunlight falling on cities. Can fossil energy change climate locally? Currently, energy use is increasing at 3 % per year. If this continues, how much energy will be used in the year 2100?
376. The surface of the sun is 5780 K. Calculate the wavelength of the maximum of its blackbody emission spectrum.
377. What is the definition of climate forcing? Give three examples of climate forcing agents.
378. Give a qualitative comparison of the transmittance, reflectance and absorptance of a cloud for visible and infrared light.
379. Compare the left and right panels of Figure 10.1. Write the formulae that explain the changes in the wavelength of the maximum and the integrated area under the curves.
380. Why does the global warming potential (GWP) of a gas depend on the 'time horizon'? (For example, Table 10.3 uses a 100 a time horizon). If a 10 a time horizon was used, would the GWP of methane increase or decrease?
381. Name six important greenhouse gases.
382. Consider Figure 10.3. What is the insolation in Copenhagen (55° 40' N latitude) on the shortest day of the year, the longest day, and on the fall and spring equinoxes?
383. Why does ozone have both a warming and a cooling role in Table 10.4? Why has the amount of ozone in the troposphere and stratosphere changed due to human activity?
384. Explain the difference between the direct and the indirect aerosol albedo effects.
385. Why do the CFC replacements (HFCs, Table 10.5) have a low GWP relative to the CFCs?

Questions for *Chemistry and the Environment*

General problems

386. Water whose only contaminant is glutathione flows into a biological wastewater treatment plant.

$^{-}OOC-CH(NH_3^{+})-CH_2)_2-CO-NH-CH(SH)-CO-NH-COOH$

Glutathione, γ-glutamylcysteinylglycine; $C_{10}H_{17}O_6N_3S$; $M = 307.30$ g/mol.

In the plant glutathione is oxidized by aerobic microorganisms at pH 6. These nitrify but do not oxidize the mercapto group; however, under the conditions of the process, atmospheric oxygen oxidizes this group to free sulfur. The reaction equations for the two processes are:

$$C_{10}H_{17}O_6N_3S + (29/2)O_2 \rightarrow 10CO_2 + 3NO_3^- + 6H_2O + H_2S + 3H^+ \quad (1)$$

$$H_2S + (1/2)O_2 \rightarrow (1/8)S_8 + H_2O \quad (2)$$

a Calculate the maximum biological oxygen demand, w_{bo}, given as the mass ratio $w_{box} = m(O_2)/m(C_{10}H_{17}O_6N_3S)$ from eq 386.1 and the total oxygen demand, w_{TOD}, given analogously from eqs 386.1 and 386.2.

In order to determine the chemical oxygen demand, w_{COD}, a certain mass of glutathione was weighed and treated with a warm, acidic (sulfuric acid) solution containing a known amount of potassium dichromate. The surplus dichromate was determined using iodometric titration, *i.e.* potassium iodide was added to reduce the dichromate to chromium(III) and the product iodine was determined by titration with a potassium thiosulfate solution of known contration.

b Write the reaction equations.

c Calculate the chemical oxygen demand, w'_{COD}, specified as the ratio $w'_{COD} = m(O_2)/m(C_{10}H_{17}O_6N_3S)$, where the numerator is the mass of oxygen that is chemically equivalent to the amount of dichromate used.

The w_{COD} of the discharged water was determined by treating samples with potassium dichromate in sulfuric acid as described above. Here w_{COD} is defined as the ratio of the mass of consumed oxygen to the mass of the sample: $w_{COD} = m(O_2)/\ m(\text{sample})$. The water (mass density 1.0 g/ml), which was only contamined by glutathione, had $w_{COD} = 238\times10^{-6}$.

d Calculate the mass of glutathion per cubic meter of water.

The flux of the discharged water was 250 m^3/d (1 d = 24 h) and the water treatment plant was designed to ozidize 75 % of the glutathion.

e Calculate the amount of oxygen which must be supplied per day.

387. The present problem is concerned with methods for determing two properties of water that are important to life, namely ***i*** the content of oxygen avaible in natural waters and ***ii*** the content of oxygen consuming contaminants in waste waters.

i Winkler's prescription for the determination of oxygen in water is a titrimetric method: A surplus of freshly prepared manganese(II) hydroxide (reaction 1) is added to the sample; this will reduce all oxygen (reaction 2). Manganese(IV) oxide is subsequently reduced with iodide in acidic solution (reaction 3), and the liberated iodine is titrated by thiosulfate (reaction 4).

$$\mathrm{Mn^{2+}(aq) + 2HO^- \rightarrow Mn(OH)_2 \cdot aq(s)} \tag{1}$$

$$\mathrm{Mn(OH)_2 \cdot aq(s) + \tfrac{1}{2}O_2 \rightarrow MnO_2 \cdot aq(s) + H_2O} \tag{2}$$

$$\mathrm{MnO_2 \cdot aq + 2I^- + 4H^+ \rightarrow Mn^{2+} + I_2(aq) + 2\,H_2O} \tag{3}$$

$$\mathrm{I_2(aq) + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-} \tag{4}$$

A sample of river water, collected at 9.5 °C, was analysed at this temperature according to Winkler's method, the result being that 1.000 kg of water used 12.80 ml 0.1000 M of a solution of sodium thiosulfate.

a Calculate the mass fraction and the molal concentration of oxygen in the water sample.

ii The content of oxygen consuming nutrients (for micro organisms) in wastewater may be determined as a mass fraction, namely the mass of oxygen used for the oxidation of all organic matter in a sample, divided by the mass of the sample. This number, the chemical oxygen demand, COD, is defined as the ratio

$$w_{\mathrm{COD}} \overset{\mathrm{def}}{=} \frac{m(\mathrm{O_2})}{m(\mathrm{sample})}$$

We will assume that the organic material has a chemical composition corresponding to the formula $\mathrm{C_{18}H_{19}O_9N}$. It is oxidized quantitatively using an acidic solution of permanganate according to the reaction equation:

$$\mathrm{5C_{18}H_{19}O_9N + 70MnO_4^- + 215H^+ \rightarrow 90CO_2 + 70Mn^{2+} + 5NH_4^+ + 145H_2O}$$

A sample of wastewater was analysed and the mass fraction of organic matter was found to be 141.6 mg/kg.

b Calculate w_{COD}.

388. Phenols are poisonous substances used as biocides. Phenol itself is widely used as a disinfectant in hospitals, and phenol and its derivatives are used in plastics, to conserve wood and as antioxidants and stabilizers in food, gasoline, lubricating oils, rubber *etc*.
The Total Oxygen Demand, w_{TOD} is determined by burning phenol at 900 °C.

a Complete the reaction equation

$$C_6H_5OH + O_2 \rightarrow CO_2 + H_2O \qquad (1)$$

and calculate the Total Oxygen Demand, w_{TOD}.

In order to determine the Chemical Oxygen Demand, w_{COD}, a measured amount of phenol is treated with surplus of potassium dichromate in sulfuric acid and the surplus is determined by titration with iron(II).

b Complete the reaction equations:

$$C_6H_5OH + Cr_2O_7^{2-} + H^+ \rightarrow CO_2 + Cr^{3+} + H_2O \qquad (2)$$

$$Cr_2O_7^{2-} + Fe^{2+} + H^+ \rightarrow Cr^{3+} + Fe^{3+} + H_2O \qquad (3)$$

In an experiment 101.0 mg of a sample containing phenol and non-oxidable impurities was treated using 1.4973 g of potassium dichromate as described above and the surplus of dichromate was titrated using 7.50 ml 0.1000 M of an iron(II) solution.

c Calculate the Chemical Oxygen Demand, w_{COD}.

A sample of wastewater contained phenol as the only contamination. Through a procedure as described above the Chemical Oxygen Demand was determined: $w_{\text{COD}} = 200\times10^{-6}$.

d Calculate the concentration of phenol in the wastewater.

389. Glyphosate is broad spectrum herbicide with only a few adverse effects. In 2001 it made up 30 % of the Danish consumption. In this problem a few chemical properties will be presented which are considered important for its behaviour in soil and ground water. The trade name of glyphosate is 'Roundup' (Monsanto).

Data for glyphosate

1 Glyphosate is *N*-(phosphonomethyl)glycine, $(HO)_2P(O){-}CH_2{-}NH{-}CH_2{-}COOH$

molar mass: $M = 169.1$ g/mol

2 Glyphosate is a trivalent acid which may accept an additional hydron. Using the abbreviation $C_3H_8NO_5P \equiv H_3L$ the four acid-base equilibria may be written:

$$H_4L^+ \overset{pK_0}{\rightleftharpoons} H_3L \overset{pK_1}{\rightleftharpoons} H_2L^- \overset{pK_2}{\rightleftharpoons} H_1L^{2-} \overset{pK_3}{\rightleftharpoons} L^{3-} \qquad (1)$$

The acidity exponents are

$pK_0 = 0.3$; $pK_1 = 2.2$; $pK_2 = 5.5$; $pK_3 = 10.1$

Here K_1, K_2, and K_3 refer to the acidity constants for the species which have lost 1, 2 and 3 hydrons, respectively. K_0 is the acidity constant for the monocation which has accepted one hydron.

3 In nature glyphosate is broken down through either (1) enzymatic hydrolysis to glycine (via sarcosine) and phosphate or (2) through an oxidative hydrolysis to glyoxylate and (aminomethyl)phosphonate (abbreviated AMPA). A summary of the metabolites including their acidity constants follows:

glycine = aminoacetic acid, $NH_2\cdot CH_2\cdot COOH$		$pK_0 = 2.3$;	$pK_1 = 9.6$
sarcosine, *N*-methylglycine, $CH_3\cdot NH\cdot CH_2\cdot COOH$		$pK_0 = 2\ 3$;	$pK_1 = 10.1$
glyoxyl acid, oxoethane acid, $HC(O)\cdot COOH$		$pK_1 = 3.2$	
AMPA, (aminomethyl)phosphonic acid, $(HO)_2P(O)\cdot CH_2\cdot NH_2$	$pK_0 = -0.4$;	$pK_1 = 5.4$;	$pK_2 = 10.1$
phosphoric acid, H_3PO_4	$pK_1 = 2.1$;	$pK_2 = 7.2$;	$pK_3 = 12.3$

4 Glyphosate forms complexes with metal ions in the soil. Formation constants for the reaction

$$M^{z+} + L^{3-} \rightleftharpoons ML^{(z-3)-}$$

are given in the table:

M^{z+}	Ca^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Fe^{3+}	Al^{3+}
$\lg \{K_{ML} / \mathrm{M}^{-1}\}$	3.3	5.5	6.9	7.2	8.1	11.9	8.7	7.3	16.1	13.7

Solubility products for hydroxides of iron(II), iron(III) and Al(III) are:

$$L_{Fe(OH)_2} = 8.0 \times 10^{-15}\ \mathrm{M}^3; \quad L_{Fe(OH)_3} = 1.0 \times 10^{-38}\ \mathrm{M}^4; \quad L_{Al(OH)_3} = 1.0 \times 10^{-34}\ \mathrm{M}^4$$

The ion product of water is $K_w = [H^+][HO^-] = 10^{-14}\ \mathrm{M}^2$.

Questions

a The chemical oxygen demand, COD, was determined by chemical oxidation which gave ammonium methylphosphonate and carbon dioxide. In principle the oxidant is oxygen(0). Calculate w_{COD}.

b The biological oxygen demand, BOD, was determined by bacterial oxidation which gave - methylphosphonate(1–), nitrate and carbon dioxide. In principle the oxidant is oxygen(0). Calculate w_{BOD}.

c A sample of groundwater (pH = 5.5) contains 5 μmol/l of glyphosate.
Calculate the BOD of the groundwater, w'_{BOD}.

d Rewrite each of the four equilibria of eq 1 such that one can clearly see the position (on the glyphosate molecule) of the hydron that enters each particular equilibrium.

e In *one* drawing, show the formation curve of each derivatives of glyphosate in the pH range $0 \leq \mathrm{pH} \leq 14$.

Mark five characteristic points on the curves and write the pH value for each.

f Strong base is added to a 0.01 M aqueous solution of glyphosate until the alkalinity has reached the value 0.03 M. Calculate pH in the final solution.

A strong acid is added dropwise until pH = 3. Sketch the variation of the buffer value during the addition.

g Write balanced reaction equations for the two reactions mentioned in point **3** above, assuming that they take place in a solution, buffered at pH = 7.

h Discuss whether iron(III) hydroxide can be dissolved (through complex formation) in a solution of glyphosate at pH = 7. Hint: Calculate an appropriate equilibrium constant.

i Explain the fact that glyphosate is retained in soils that are rich on hydroxides of aluminium and iron(III), but not in soils which only contain quartz.

j Discuss whether the data shown in table *4* vary according to known empirical rules.