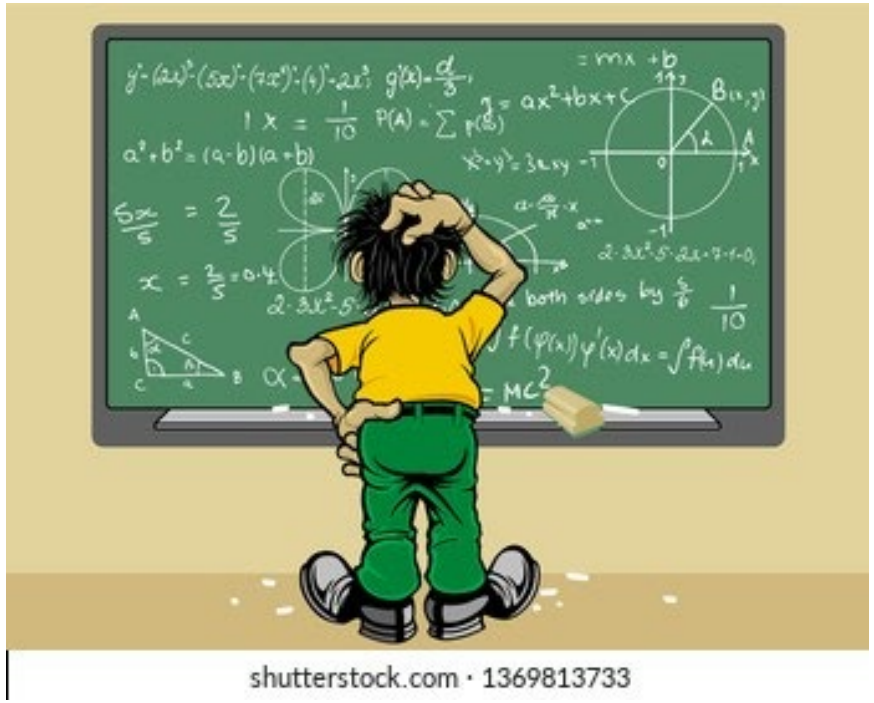


General Revision 2024

Exercises on your choice of topic:

- Carbonate and alkalinity
- Redox
- Metal solubility and complexation
- Kinetics
- Partitioning

1. pH and alkalinity of drinking water

a) An open drinking water reservoir contains pure water in equilibrium with the atmosphere at 25 °C (open system). What are the pH and alkalinity of this water?

b) To use this water as drinking water, its temperature has to be lowered to 10 °C. What is the pH of this water now?

c) To use this water as drinking water, you need to adjust its alkalinity and pH. To do so, you move the water from the open to a closed reservoir (closed system). You want to reach an alkalinity of around 2.5 mM and a pH around 8.5. What strategy would you use to adjust the pH and alkalinity?

d) Once the T, pH and alkalinity are adjusted, you now distribute the water from exercise c) into households. The distribution system consists of iron pipes. In the iron pipes, the water is in equilibrium with siderite ($FeCO_3$; pK_s ($FeCO_3$) = 10.5 at 10 °C). What is the pH of the water inside the pipe (closed system)?

2. Rain falling on dinosaurs

a. As we have seen in class, the current partial pressure of CO_2 in the atmosphere is ca. $10^{-3.37}$ atm. At this level of atmospheric CO_2, what is the pH of a raindrop on a summer day of 25 °C?

b. It is well-known that the CO_2 content of the atmosphere, as well as the average global temperature, have fluctuated throughout the ages. For example, during the Jurassic period, dinosaurs were exposed to 7-fold higher atmospheric CO_2 levels, and significantly higher temperatures. What was the pH of a raindrop during the Jurassic period on a summer day of 40 °C?

c. During the Jurassic period, the earth also had a lot of active volcanos, which emitted large amounts of SO_2 (sulfur dioxide, a gas) into the atmosphere. When SO_2 dissolves in water, it forms sulfurous acid:

$SO_2 + H_2O \leftrightarrow H_2SO_3$ $\quad pK_H$ (40 °C) = 0.13

$H_2SO_3 \leftrightarrow HSO_3^- + H^+$ $\quad pK_{a1}$ (40 °C) = 1.8

$HSO_3^- \leftrightarrow SO_3^{2-} + H^+$ $\quad pK_{a2}$ (40 °C) = 6.9

Assume that the partial pressure of SO_2 after a volcano eruption is 10^{-5} atm. What is the pH of rain after the eruption?

d. A little snail lives among the dinosaurs. The snail has a house that is made entirely of $CaCO_3$. After a volcanic eruption, the snails' house begins to dissolve (poor snail!). How much more Ca^{2+} can be dissolved in the rain after a volcanic eruption, compared to the rain before the eruption? You can assume that the dissolution of snail houses does not affect the pH of the rain water.

If you didn't find the pH values of rain, make an assumption!

3. Cadmium in wastewater

Cadmium is a toxic metal which can be found in relatively high concentrations in municipal wastewater effluents. Its toxicity depends on the cadmium speciation, wherefore, it is important to assess in which form it is present in wastewaters. The following (simplified) equilibria are given:

β-$Cd(OH)_2 + 2H^+ \Leftrightarrow Cd^{2+} + 2H_2O$ $\quad \log K^*_{so} = 13.65$

$Cd^{2+} + H_2O \Leftrightarrow Cd(OH)^+ + H^+$ $\quad \log K_1 = -10$

$Cd^{2+} + 2H_2O \Leftrightarrow Cd(OH)_2 + 2H^+$ $\quad \log K_2 = -20$

$Cd^{2+} + 3H_2O \Leftrightarrow Cd(OH)_3^- + 3H^+$ $\quad \log K_3 = -33$

$Cd^{2+} + 4H_2O \Leftrightarrow Cd(OH)_4^{2-} + 4H^+$ $\quad \log K_4 = -47$

a) Derive the equations for the pH dependence of the Cd species and plot them in the graph below.

b) Which Cd(II) species determines Cd(II) solubility at pH 7 and what is its concentration?

c) Cd(II) can be complexed by bromide according to the following equilibrium:

$Cd^{2+} + Br^- \Leftrightarrow CdBr^+$ $\quad \log K_5 = 2.15$

What is the required bromide concentration to affect the cadmium speciation at pH 7? How does this compare to typical bromide concentrations in municipal wastewaters (≤ 2µM)?

4. Kinetics of bromide oxidation

HOCl, hypochlorous acid, is the major form of free chlorine in water at pH < 7.5. It reacts rapidly (second order rate constant $k_2 = 1.3 \times 10^3\ M^{-1}\ s^{-1}$) with bromide ions to form HOBr, hypobromous acid, and Cl^-:

$$HOCl + Br^- \rightarrow HOBr + Cl^-$$

A slightly acidic (pH = 6.2) ground water being used for drinking water has a bromide concentration of 80 ppb and is dosed with chlorine to yield a free chlorine residual concentration of 1 mg/L as Cl. What is the concentration of HOBr in the water after 1 minute of reaction?

(Molar mass of Br is 79.9 g/mol, molar mass of Cl is 35.45 g/mol)

5. Redox reactions of iodine

Iodide (I^-) can be a problematic compound during oxidative water treatment, because it may lead to potentially toxic iodo-organic compounds. The precursor for the formation of these compounds is hypoiodous acid (HOI). HOI may be formed during chlorination processes oxidation of iodide to HOI):

$$HOCl + I^- \rightarrow HOI + Cl^-$$

a) Calculate the redox potential of this reaction at pH 7 based on the following standard reduction potentials. What is the pH dependence of the redox potential of the net reaction?

$$HOCl + H^+ + 2e^- \rightarrow Cl^- + H_2O \qquad E^0 = 1.49\ V$$

$$HOI + H^+ + 2e^- \rightarrow I^- + H_2O \qquad E^0 = 0.99\ V$$

b) Once HOI is formed during chlorination, its stability has to be assessed in later treatment steps. For several treatments, hydrogen peroxide is added and may reduce HOI back to I^-. Is the reduction of HOI a thermodynamically favorable process at pH 7?

$$HOI + H^+ + 2e^- \rightarrow I^- + H_2O \qquad E^0 = 0.990\ V$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad E^0 = 0.682\ V$$

6. EDTA speciation in wastewater

EDTA is a common ligand which is widely applied in industry and household products such as textile washing detergents. Therefore, significant concentrations can be detected in municipal wastewater treatment plants. With the implementation of ozonation for enhanced wastewater treatment, the fate of EDTA becomes an important issue, because its discharge to the environment should be avoided.

In this question, only three EDTA species are considered, namely $EDTA^{4-}$, $HEDTA^{3-}$ (pK_a = 10.3) and H_2EDTA^{2-} (pK_a = 6.2). In the following the charges are omitted for simplicity.

a) Calculate the EDTA speciation (concentrations of EDTA, HEDTA, H_2EDTA) at pH 7 for a total EDTA concentration of 1 µM.

b) The raw water that is treated with ozone also has an iron(III) (Fe(III)) concentration of 0.5 µM. This affects the EDTA speciation because of the strong complexation of Fe(III) (logK (Fe(III) + EDTA) = 25.1). Calculate the speciation of EDTA for the conditions in the raw water ($[EDTA]_{tot}$ = 1 µM, $[Fe(III)]_{tot}$ = 0.5 µM, hint: Fe(III) will be fully complexed with EDTA: [FeEDTA] = $[Fe(III)]_{tot}$).

7. Chrysene in the golf of Mexico

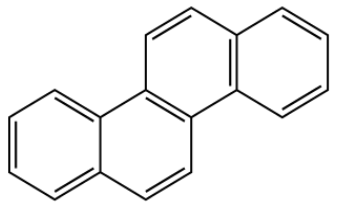
In 2010, the “Deepwater Horizon” oil spill led to a contamination of the Gulf of Mexico with approximately 500 million liters of oil. Among the compounds spilled was chrysene, a polycyclic aromatic hydrocarbon (PAH) (see figure). Like most PAHs, chrysene has strong ecotoxicological effects, therefore its presence in water is problematic. Chrysene has low water solubility (C_w^{sat}= $10^{-8.05}$ M), and an intermediate vapor pressure (p_L*= $10^{-6.22}$ Pa at 25 °C).

a. After the spill, a dissolved concentration of $2*10^{-9}$ M chrysene is measured. Is the salty seawater saturated in chrysene? Assume that the seawater temperature and the air temperature are both 25 °C.

b. One way to remove chrysene from water is to evaporate it into air. How much air would have to be bubbled through 1 L of seawater to transfer half of the chrysene into air?

c. Another possibility to remove chrysene is to add octanol to the water, let the chrysene partition into the octanol, and then remove the octanol along with the extracted chrysene. How much octanol would have to be added to 1 L of seawater to transfer half of the chrysene into octanol?

d. To speed up the chrysene removal process, you decide to increase the temperature. How will this affect the transfer of chrysene into air (exercise b) or octanol (exercise c)? Give a qualitative answer, and explain your reasoning.



Structure of chrysene

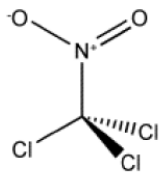
8. Partitioning and decay of chloropicrin

Chloropicrin (CP) is a volatile pesticide, which is applied against insects on various crops. It's structure and some known physical-chemical parameters are given below.

a. A farmer would like to grow tomatoes, strawberries and almonds, but she is concerned about the CP content in these plants. CP is typically applied in the air, and then partitions into the plants and the soil. Using the information provided in the table below, estimate which plant will contain the most CP at equilibrium. Give a qualitative answer (no calculation is necessary but explain your reasoning).

b. To not use too much CP, the farmer decides that it is a good approach to grow the tomatoes in a small, rectangular greenhouse. The greenhouse has a surface area of 20 m^2 and a height of 5.5 m. The farmer fills the first 0.5 m with soil that has an organic carbon content of 30%, a density of 2 kg/L and a porosity of 0.5 (meaning that half of the volume is soil and half is air). Finally, she grows the tomatoes. When the total dry weight of tomatoes is 5 kg, the farmer applies CP. What is the fraction of CP in the tomatoes at equilibrium?

c. If CP enters a surface water, it is rapidly removed by volatilization and by photolysis (reaction with sunlight). Both processes are first order in CP, and have similar half-lives ($t_{1/2}$ for volatilization = 4.3 days, $t_{1/2}$ for photolysis = 3 days). How long will it take for the concentration of CP to decay to 10% of its initial concentration?



Chloropicrin

C_w^{sat}= 0.012 M

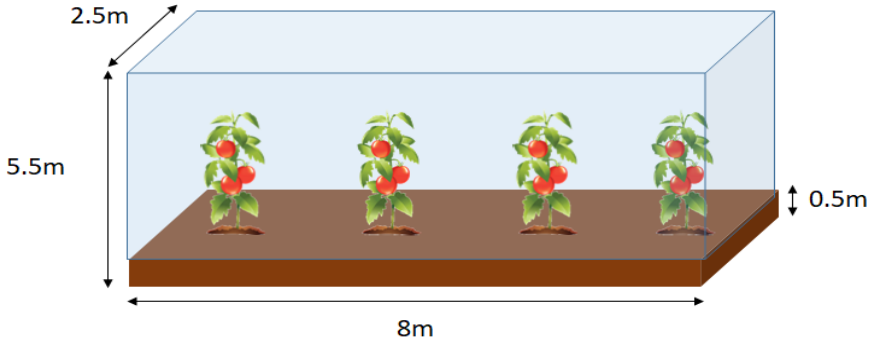
p_L^*= 0.03 atm

K_{ow} = 54

$K_{tomato\text{-}water}$ = *7.9 L water / kg dry weight*

Composition of some fruit and nuts (in % of dry weight):

	Tomato	Strawberry	Almond
Carbohydrates	78	89	22
Lipids	4	4	56
Proteins	18	10	21

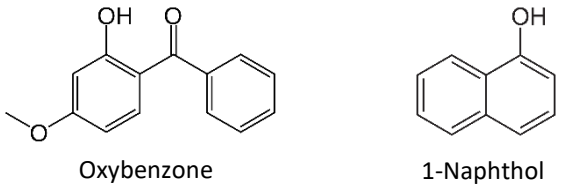


9. Fate of oxybenzone in sea water

Oxybenzone is a widely used ingredient of sunscreen and helps prevent sunburn of human skin. Unfortunately, recent research has shown that oxybenzone contributes to the bleaching and destruction of coral reefs. For at least one type of coral, an aqueous oxybenzone concentration of 62 ng/L can lead to coral death within 4 hours. To avoid coral deaths, it is important to understand the concentration and fate of oxybenzone in the marine environment. You have done some research on oxybenzone and sunscreen. You have found that on average, 1 g of sunscreen contains 0.03 g of oxybenzone, and that the density of sunscreen is 1 g/cm^3. Furthermore, you found the following information:

- Molecular weight of oxybenzone: 228.2 g/mol
- Log K_{ow} of oxybenzone: 3.6
- Log K_{aw} of oxybenzone: -4.8
- The environmental behavior of oxybenzone is similar to that of 1-natphthol, a polycyclic aromatic hydrocarbon (see Figure)
- The solvent properties of sunscreen are comparable to those of octanol

a. What is the solubility of oxybenzone in seawater?
b. To avoid sunburn, an adult is recommended to apply 30 g of sunscreen on his/her body. What volume of seawater is needed to dissolve 90% of the oxybenzone from the sunscreen while swimming in the sea?
c. Assuming one swimmer per 10 m^3 of seawater, what will be the concentration of oxybenzone, and will it be above or below the toxicity level of 62 ng/L? You can assume partitioning equilibrium between oxybenzone in seawater and in the sunscreen.



Oxybenzone 1-Naphthol

Structures of oxybenzone and 1-naphthol