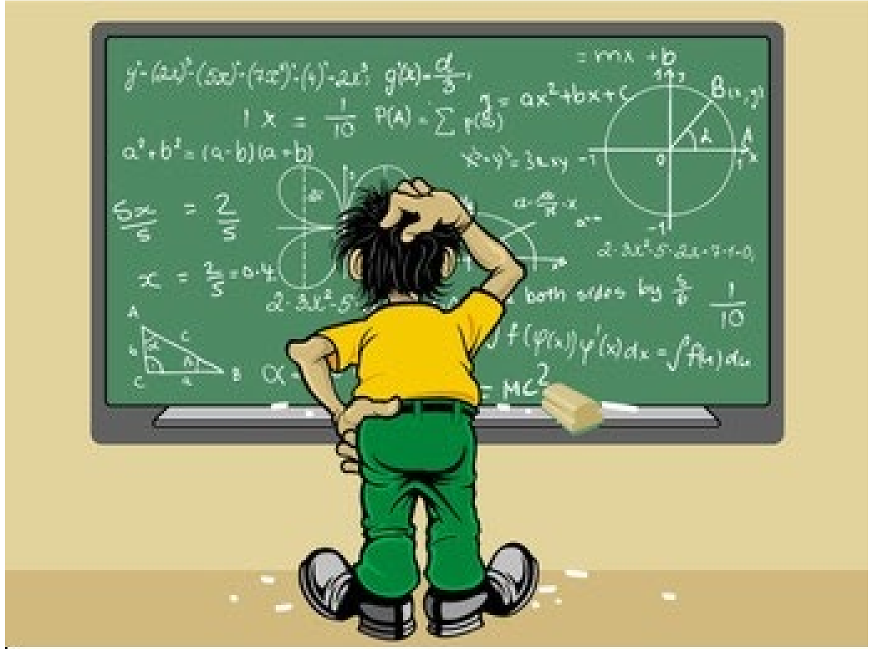
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General Revision 2024

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)?

1. pH and alkalinity of drinking water

solutions

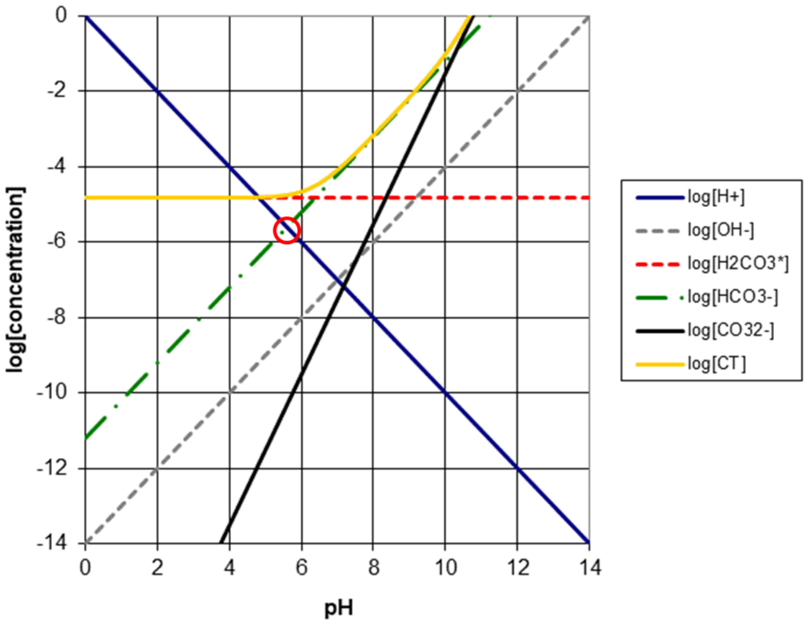
a) An open drinking water reservoir contains pure water in equilibrium with the atmosphere at 25 °C (open system). What are the pH and alkalinity of this water?

The pH of pure water in equilibrium with the atmosphere is 5.6.

Alk = $[HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-] - [H^+]$.

At pH 5.6, $[HCO_3^-]=[H^+]$, and $[CO_3^{2-}]$ and $[OH^-]$ are very small. So Alk = 0.

We can also figure this out another way : Alk inidicates the extent by which the system is deficient in protons to to convert all CO_3^{2-} and HCO_3^- to H_2CO_3. Because in pure water H_2CO_3 (as CO_2 from the atmosphere) is the only source of carbonate, no proton-deficient carbonate was added to the system, so the system is not deficient in protons at all.



1. pH and alkalinity of drinking water

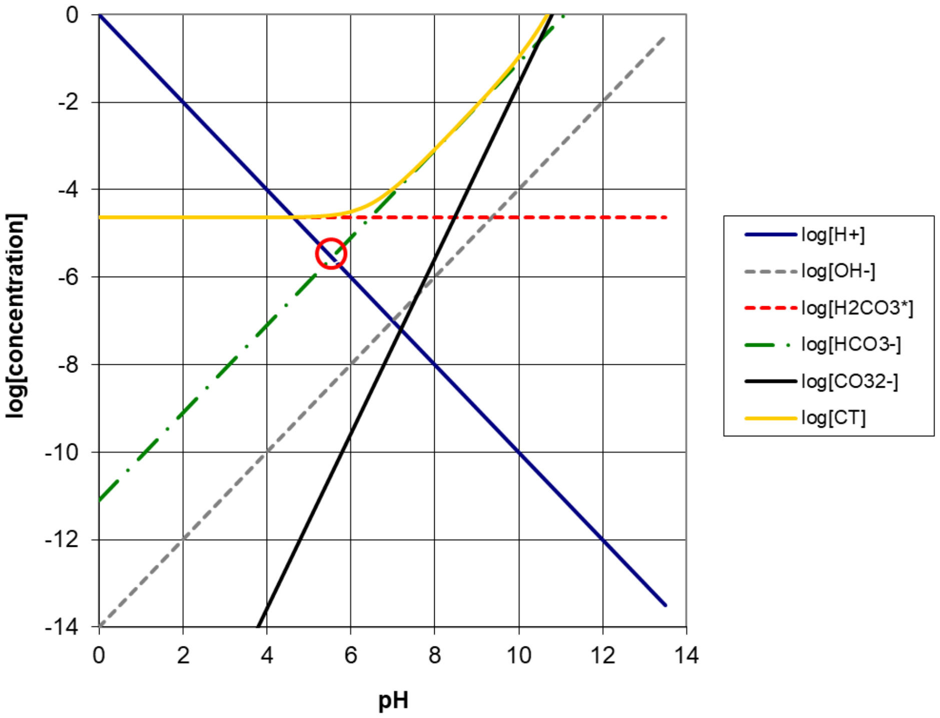
solutions

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?

To answer this question, we re-draw the graph from above, but using equilibrium constants adjusted to 10 C. From the table on slide 7 of the carbonate notes, and from the acid-base notes, we find:

$pK_H = -1.27$; $pK_{a1} = 6.46$; $pK_{a2} = 10.49$, $pK_w = 14.53$.

Using these constants, the graph from 1a) changes as follows:
$\log[H_2CO_3] = \log [p_{CO2}]+pK_H = -3.37-1.27 = -4.64$
$\log[HCO_3^-]=-pKa_1+pH+\log \log[H_2CO_3]=-6.46+pH-4.77 = -11.23+pH$
$\log[CO_3^{2-}]=-^{-}]=-pKa_2+pH+\log \log[HCO_3^-]=-21.72+2pH$
$\log[OH^-]=pK_w -pH = 14.53-pH$



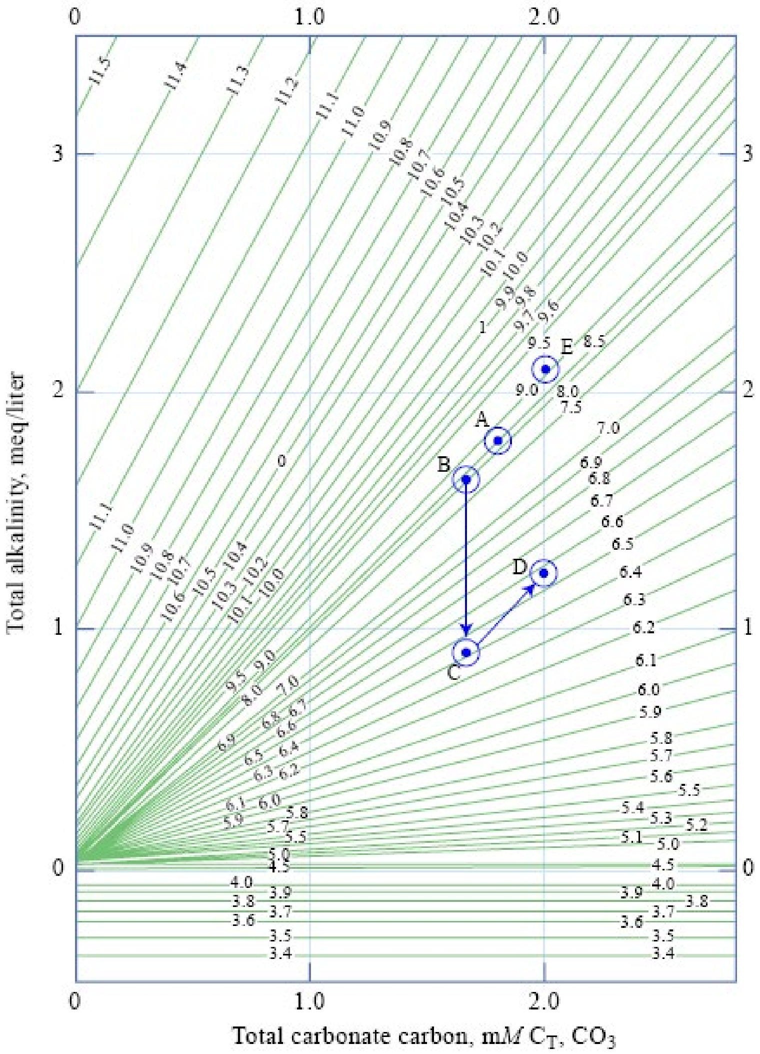
The change in pH is minimal, it remains about 5.6. This is because the temperature had two opposing effects: on the one hand, the pK_a values increased a little bit at lower temperatures, making carbonic acid and bicarbonate less acidic. On the other hand, more CO_2 dissolves into the water at lower temperature, adding more acid to the system.

1. pH and alkalinity of drinking water

solutions

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?

To raise the alkalinity to 2.5 mM, we can either add 2.5 mM of HCO_3^- or 1.25 mM of CO_3^{2-}. This will also increase the pH. According to Deffeye's diagram, addition of 2.5 mM HCO_3^- results in a pH of approximately 8.5, which is what we want. In contrast, addition of 1.25 mM CO_3^{2-} results in a pH above 10. This means that we would then need to add a strong acid to lower the pH back to 8.5.



1. pH and alkalinity of drinking water

solutions

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)?

Draw a graph for a closed carbonate system in equilibrium with siderite at 10 C.

At pH 8.5, $C_T \approx [HCO_3^-]$. Furthermore, at pH of 8.5, we also know that $[Alk] \approx [HCO_3^-]$. So $[HCO_3^-] \approx C_T = 2.5$ mM.

Then, we need to draw a line for Fe^{2+} on the graph:

$[Fe^{2+}][CO_3^{2}]=K_s$, so $\log[Fe^{2+}] = -pK_s - \log[CO_3^{2}] = -pK_s - \log(C_T\alpha_2)$

The line for Fe^{2+} is easily drawn by recognizing that at any point in the graph,

$\log[CO_3^{2}] + \log[Fe^{2+}]$ =const. So the two lines are mirror images.

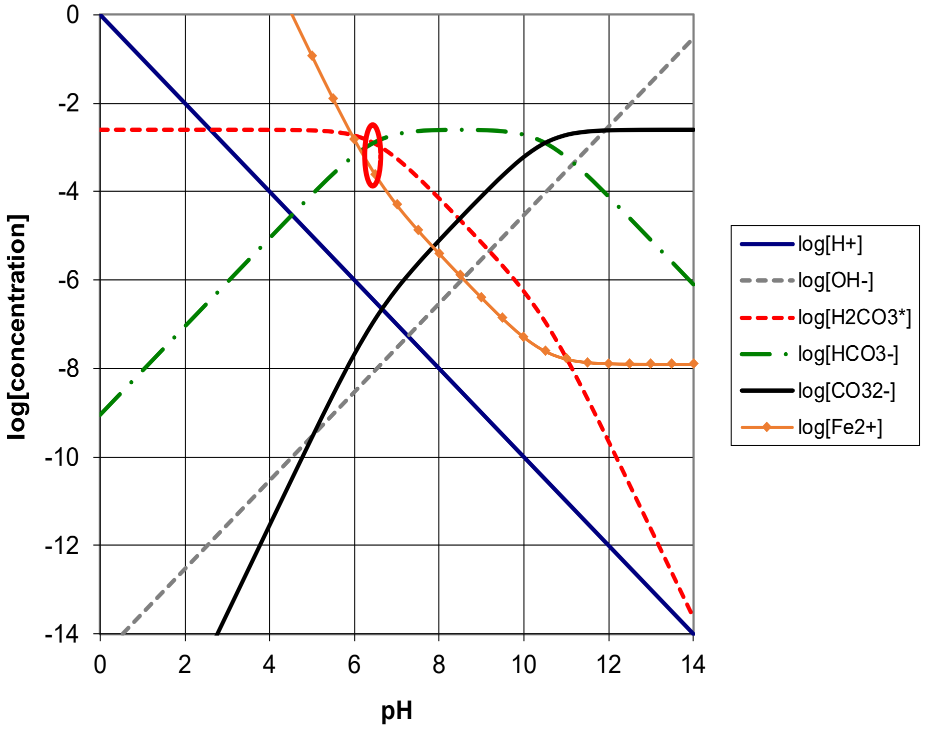
In equilibrium with siderite, the following charge balance applies:

$[H^+] + 2\,[Fe^{2+}] = [OH^-] + [HCO_3^-] + 2\,[CO_3^{2-}]$.

Recognizing that for most of the pH range $[Fe^{2+}] >> [H^+]$, and $[HCO_3^-] >> [OH^-]$, $[CO_3^{2-}]$, we can simplify :

$2\,[Fe^{2+}] = [HCO_3^-]$ or $\log[Fe^{2+}] + 0.3 = \log[HCO_3^-]$.

The equilibrium pH is thus around 6.3.



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:

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

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

$HSO_3^- \leftrightarrow SO_3^{2-} + H^+$ 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!

2. Rain falling on dinosaurs

solutions

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? 5.6

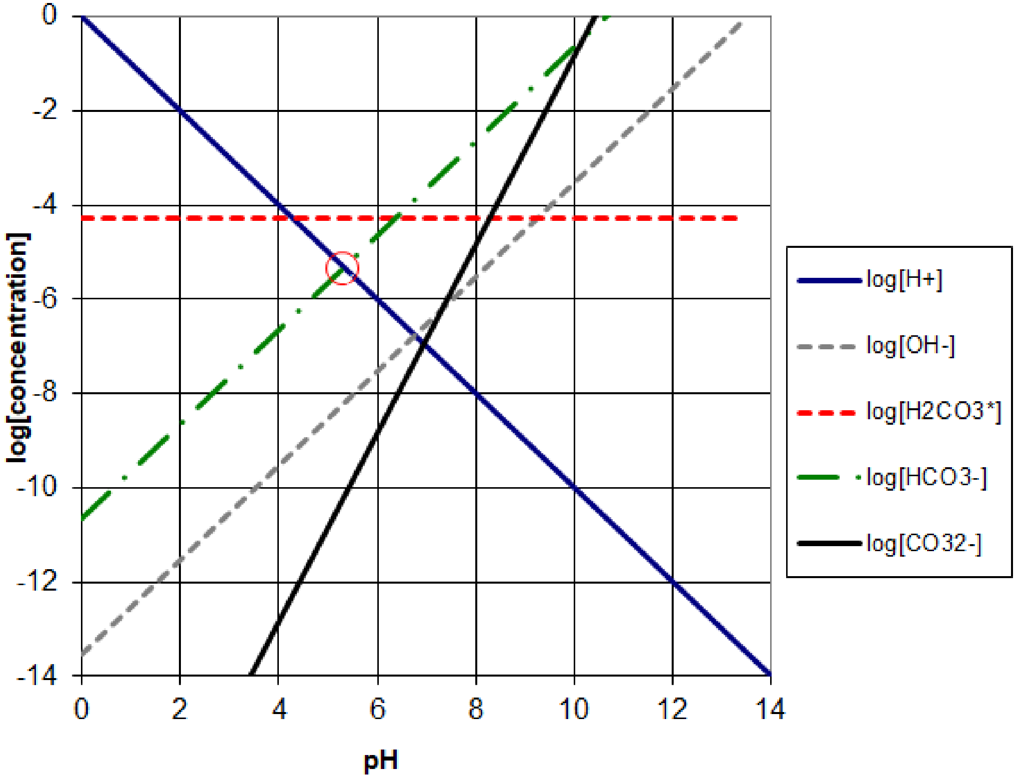
b. It is well-known that the CO_2 content of the atmosphere, as well as the average global temperature, have fluctuated throughout the ages. For example, during the Jurassic period, dinosaurs were exposed to 7-fold higher atmospheric CO_2 levels, and significantly higher temperatures. What was the pH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

	pK (I=0)					
Reaction	5 °C	10 °C	15 °C	20 °C	25 °C	40 °C
$CO_2(g) + H_2O \leftrightarrow H_2CO_3^*$	-1.20	-1.27	-1.34	-1.41	-1.47	-1.64
$H_2CO_3^* \leftrightarrow H^+ + HCO_3^-$	6.52	6.46	6.42	6.38	6.35	6.35
$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$	10.56	10.49	10.43	10.38	10.33	10.22
$H_2O \leftrightarrow H^+ + OH^-$	14.73	14.53	14.34	14.16	14.0	13.53
$CaCO_3(s) \leftrightarrow Ca^{2+} + CO_3^{2-}$	8.35	8.36	8.37	8.39	8.42	8.53

$$\log[H_2CO_3^*] = \log[p_{CO_2}] + pK_H$$

$$\log[HCO_3^-] = -pK_1 + pH + \log[H_2CO_3^*] = -pK_1 + pH + \log[p_{CO2}] + pK_H$$

$$\log[CO_3^{2-}] = -pK_2 + pH + \log[HCO_3^-] = -pK_2 - pK_1 + 2pH + \log[p_{CO2}] + pK_H$$



pH = 5.5

2. Rain falling on dinosaurs

solutions

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:

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

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

$HSO_3^- \leftrightarrow SO_3^{2-} + H^+$ 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?

We need to add the SO_2 system to the plot, exactly analogously to the CO_2 system. We add the following lines:

$\log[H_2SO_3]=\log[p_{SO2}]+pK_{H,SO2}= -5+0.13= -4.87$

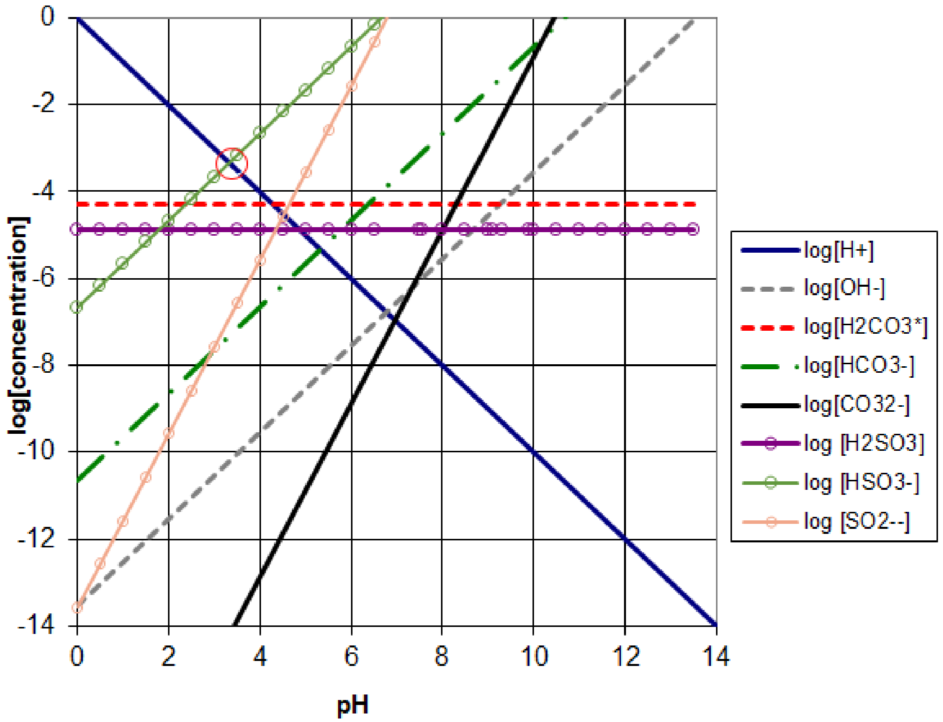
$\log[HSO_3^-]= -pK_{a1} + pH+ \log[p_{SO2}]+pK_{H,SO2}= -6.67 + pH$

$\log[SO_3^{2-}]= -pK_{a2}-pK_{a1} + 2pH + \log[p_{SO2}]+pK_{H,SO2}= - 13.57 + 2pH$

The new mass balance must account for the fact that we have an additional acid present, added as H_2SO_3:

$[H^+] = [HCO_3^-] + 2[CO_3^{2-}]+ [HSO_3^-]+2[SO_3^{2-}]+ [OH^-]$

In our system, we can simplify to: $[H^+] \approx [HSO_3^-]$, and we find that the new pH of rain is ca. 3.5.



2. Rain falling on dinosaurs

solutions

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!

The CO_3^{2-} concentration of the "normal" rain (pH 5.5) is about 10^{-10} M (either from the plot, or by calculation, using

$$\log[CO_3^{2-}] = -pK_{a2} - pK_{a1} + 2pH + \log[p_{CO2}] + pK_{H,CO2}$$

The CO_3^{2-} concentration after the eruption (pH 3.5) decreases by a factor 10^4 (per pH unit decrease, the CO_3^{2-} concentration decreases by 2 log units).

Furthermore, we know that $K_{S,\,CaCO3} = [Ca^{2+}][CO_3^{2-}]$. So if the CO_3^{2-} concentration decreases by a factor of 10^4, then we can increase the Ca^{2+} concentration in solution by a factor of 10^4. After the volcanic eruption, we can thus dissolve 10'000 more Ca^{2+} in the rain water. That is bad news for the snail.

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:

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

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

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

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

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

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:

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

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)?

3. Cadmium in wastewater

solutions

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

For Cd^{2+}:

$$\frac{[Cd^{2+}]}{[H^+]^2} = K'_{so} = 10^{13.65} \Rightarrow [Cd^{2+}] = [H^+]^2 K'_{so}$$

$$\log([Cd^{2+}]) = \log K'_{so} - 2pH = 13.65 - 2pH$$

For $Cd(OH)^+$:

$$\frac{[Cd(OH)^+][H^+]}{[Cd^{2+}]} = 10^{-10}$$

$$[Cd(OH)^+] = [H^+] \times 10^{-10} \times 10^{13.65}$$

$$\log([Cd(OH)^+]) = 3.65 - pH$$

For $Cd(OH)_2$:

$$\frac{[Cd(OH)_2][H^+]^2}{[Cd^{2+}]} = 10^{-20}$$

$$[Cd(OH)_2] = 10^{-20} \times 10^{13.65}$$

$$\log([Cd(OH)_2]) = -6.35$$

For $Cd(OH)_3^-$:

$$\frac{[Cd(OH)_3^-][H^+]^3}{[Cd^{2+}]} = 10^{-33}$$

$$[Cd(OH)_3^-] = [H^+]^{-1} \times 10^{-33} \times 10^{13.65}$$

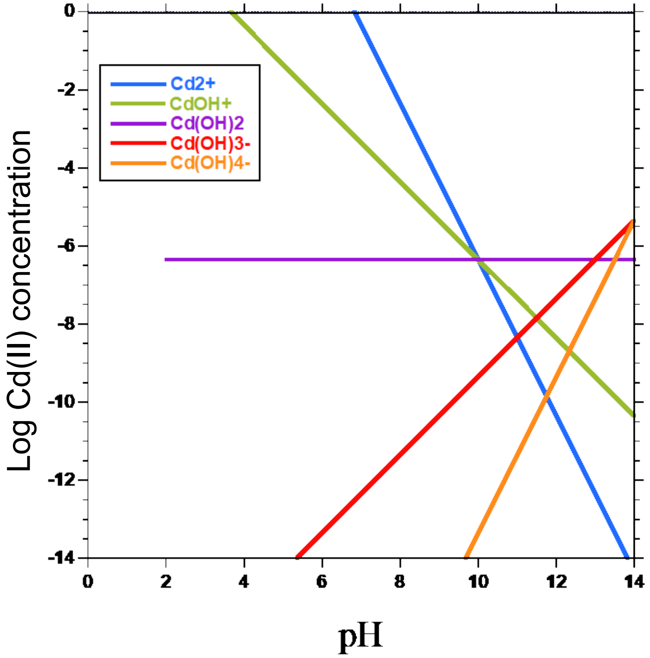
$$\log([Cd(OH)_3^-]) = -19.35 + pH$$

For $Cd(OH)_4^{2-}$:

$$\frac{[Cd(OH)_4^{2-}][H^+]^4}{[Cd^{2+}]} = 10^{-47}$$

$$[Cd(OH)_4^{2-}] = [H^+]^{-2} \times 10^{-47} \times 10^{13.65}$$

$$\log([Cd(OH)_4^{2-}]) = -33.35 + 2pH$$

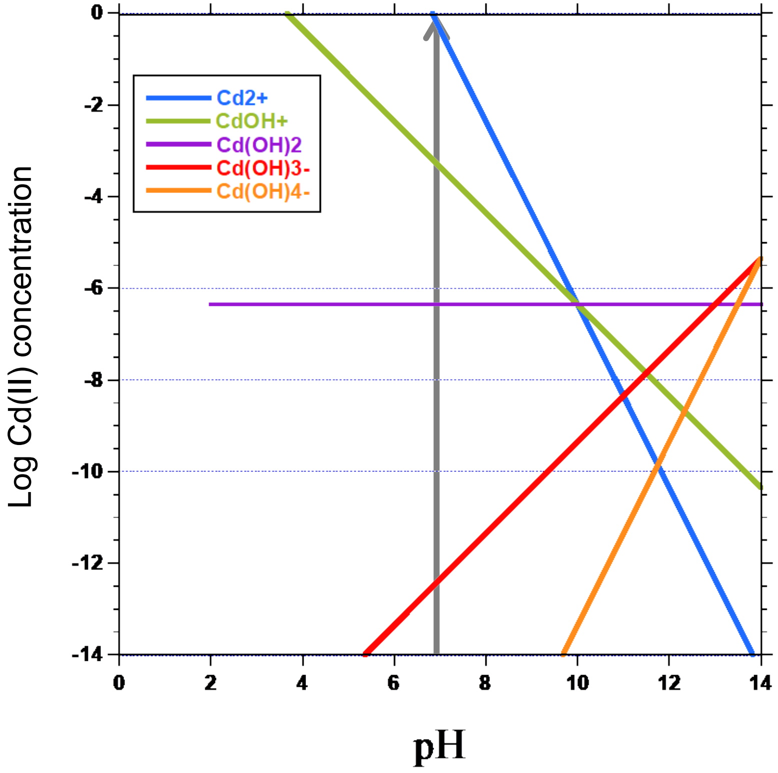


3. Cadmium in wastewater

solutions

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

Cd^{2+} dominates Cd(II) solubility at pH 7. Its concentration is around 0.45 M (log Cd(II) = -0.35).



3. Cadmium in wastewater

solutions

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

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

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)?

$$\frac{[CdBr^{+}]}{[Cd^{2+}][Br^{-}]} = 10^{2.15}$$

Solve for [CdBr^{+}] and replace [Cd^{2+}] by [H+]^{2} K^{*}_{so} (part a)

$$[CdBr^{+}] = [H^{+}]^{2} \times 10^{13.65} \times 10^{2.15}[Br^{-}]$$

Take logs

$$\log([CdBr^{+}]) = -2pH + 15.8 + \log([Br^{-}])$$

$$pH7 : \log([CdBr^{+}]) = 1.8 + \log\log([Br^{-}]) \geq -0.35$$

$$\Rightarrow [Br^{-}] \geq 7mM$$

At pH 7, log ([CdBr^{+}]) = 1.8 + log ([Br^{-}]). As we saw in part b, the log Cd^{2+} concentration is around -0.35, i.e., log ([CdBr^{+}]) would have to be at or above that level to affect Cd speciation. We can thus calculate the required Br^{-} concentration according to:

log ([CdBr^{+}]) = 1.8 + log ([Br^{-}]) = -0.35

[Br^{-}] = 7 mM which is significantly above the concentration detected in wastewater. The required bromide levels to affect the Cd(II) speciation is significantly above the concentrations detected in wastewaters. Therefore, bromide will not affect the Cd(II) speciation.

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 $k_2 = 1.3\times10^3\ M^{-1}\ s^{-1}$) 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)

4. Kinetics of bromide oxidation

solutions

$[Br^-]_0$ = 80 ppb / 79.9 g/mol = 1×10^{-6} M

1 ppb = 1 µg/L

$[HOCl]_0$ = 1 mg/L as Cl / 35.45 g/mol = 2.82×10^{-5} M

Integrated rate law for second order kinetics: $\frac{[A]}{[B]} = \frac{[A]_0}{[B]_0} e^{([A]0-[B]0)kt}$

Calculate $\frac{[A]}{[B]}$ at t = 1 min:

$$\frac{[A]}{[B]} = \frac{1 \times 10^{-6}\ M}{2.82 \times 10^{-5}\ M} e^{([1 \times 10^{-6}\ M - 2.82 \times 10^{-5}\ M)1.3 \times 1000\ M^{-1}\ s^{-1} \times 60\ s)} = 0.008$$

$\frac{[A]}{[B]} = 0.008 = \frac{[A]_0 - X}{[B]_0 - X}$ where X is concentration of $[Br^-]$ = [HOCl] that reacts in 1 min

Solve for X: $[A]_0 - X = 0.008\ [B]_0 - 0.008\ X$

$[A]_0 - 0.008\ [B]_0 = X - 0.008\ X = X\ (1-0.008)$

$X = \frac{[A]_0 - 0.008\ [B]_0}{1-0.008} = 8.2 \times 10^{-7}$ M

Around 82 % of the total Br^- reacted.

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?

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

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

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

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

5. Redox reactions of iodine

solutions

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?

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

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

For HOCl:
Nernst equation: $E = E^0 – 0.059/n \log([Cl^-]/([HOCl][H^+]))$
$E = E^0 – 0.059/2\ (7) – 0.059/2 \log([Cl^-]/[HOCl])$
Thus, $E^{0'}$ (pH 7) = 1.49 – 0.059/2 (7) = 1.28 V

For HOI: $E^{0'}$ (pH 7) = 0.99 – 0.059/2 (7) = 0.78 V

For the combined reaction (oxidation of iodide with HOCl), $E^{0'}$ equals
$E^{0'}$ ($HOCl/Cl^-$) - $E^{0'}$ (HOI/I^-) = 1.28 V - 0.78 V = 0.5 V
The pH dependence is the same for both half cell reactions (one proton is transferred per two electrons), hence, pH has no effect on the difference in potential.

5. Redox reactions of iodine

solutions

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?

$HOI + H^+ + 2e^- \rightarrow I^- + H_2O$ $E^0 = 0.990$ V
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ $E^0 = 0.682$ V

The pH dependence of the two reactions is different. Therefore, we have to formulate Nernst equations for both half reactions:

For HOI:
Nernst equation: $E = E^0 – 0.059/n \log([I^-]/([HOI][H^+]))$
$E = E^0 – 0.059/2\ (7) – 0.059/2 \log([I^-]/[HOI])$
Thus, $E^{0'}$ (pH 7) = $0.99 – 0.059/2\ (7) = 0.784$ V

For H_2O_2:
Nernst equation: $E = E^0 – 0.059/n \log([H_2O_2]/([O_2][H^+]^2))$
$E = E^0 – 2*0.059/2\ (7) – 0.059/2 \log([H_2O_2]/([O_2])$
Thus, $E^{0'}$ (pH 7) = $0.682 – 2*0.059/2\ (7) = 0.269$ V

The overall redox reaction is
$HOI + H_2O_2 = I^- + H_2O + H^+ + O_2$ $\Delta E = 0.784 – 0.269 = 0.515$ V
Since $\Delta E > 0$, the reaction is thermodynamically favorable.

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: $[FeEDTA] = [Fe(III)]_{tot}$).

6. EDTA speciation in wastewater

solutions

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

$$[EDTA]_{tot} = [EDTA] + [HEDTA] + [H_2EDTA]$$

$$\frac{[H^+][EDTA]}{[HEDTA]} = 10^{-10.3}$$

$$\frac{[H^+]^2[EDTA]}{[H_2EDTA]} = 10^{-16.5}$$

$$[EDTA]_{tot} = [EDTA]\left(1 + \frac{[H^+]}{10^{-10.3}} + \frac{[H^+]^2}{10^{-16.5}}\right)$$

$$\text{At pH 7: } 1 + \frac{[H^+]}{10^{-10.3}} + \frac{[H^+]^2}{10^{-16.5}} = 2313$$

$$[EDTA] = \frac{[EDTA]_{tot}}{2313} = 0.00043 \times [EDTA]_{tot} = 4.3 \times 10^{-10} M$$

$$[HEDTA] = \frac{[EDTA]_{tot}}{2313}\frac{[H^+]}{10^{-10.3}} = 0.86 \times [EDTA]_{tot} = 8.6 \times 10^{-7} M$$

$$[H_2EDTA] = \frac{[EDTA]_{tot}}{2313}\frac{[H^+]^2}{10^{-16.5}} = 0.14 \times [EDTA]_{tot} = 1.4 \times 10^{-7} M$$

6. EDTA speciation in wastewater

solutions

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] = $[Fe(III)]_{tot}$).

$$[EDTA]_{tot} = [EDTA]\left(1 + \frac{[H^+]}{10^{-10.3}} + \frac{[H^+]^2}{10^{-16.5}}\right) + [FeEDTA]$$

$$[EDTA] = \frac{[EDTA]_{tot} - [FeEDTA]}{\left(1 + \frac{[H^+]}{10^{-10.3}} + \frac{[H^+]^2}{10^{-16.5}}\right)} = 2.15 \times 10^{-10} M$$

$$[HEDTA] = 4.3 \times 10^{-7} M$$
$$\left[H_2EDTA\right] = 7 \times 10^{-8} M$$
$$[FeEDTA] = 5 \times 10^{-7} M$$

7. Chrysene in the golf of Mexico

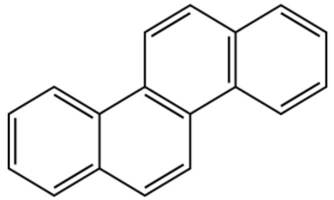
In 2010, the “Deepwater Horizon” oil spill led to a contamination of the Gulf of Mexico with approximately 500 million liters of oil. Among the compounds spilled was chrysene, a polycyclic aromatic hydrocarbon (PAH) (see figure). Like most PAHs, chrysene has strong ecotoxicological effects, therefore 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

7. Chrysene in the golf of Mexico

solutions

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.

Calculate the maximal solubility of chrysene in seawater and compare it to measured concentration.

$C^{sat}_{\text{chrysene, seawater}} = C^{sat}_{\text{chrysene,w}} *10^{-Ks[NaCl]}$.

The Setschenow constant $K^{s}_{\text{chrysene}} = 0.34\ M^{-1}$ (see slide 25), and we can assume a NaCl concentration of 0.5 M. So $K^{s}[salt] = 0.17$, and $C^{sat}_{\text{chrysene, seawater}} = 10^{-8.22}$ M

The measured concentration is lower than the maximally soluble one, so the seawater is undersaturated in chrysene.

7. Chrysene in the golf of Mexico

solutions

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?

If we transfer half of the chrysene from water to air, this means that the mass in the water phase ($C_{\text{chrysene, w}}$*V_w) must equal the mass in the air ($C_{\text{chrysene, a}}$*V_a).

Furthermore, we know that $K_{\text{chrysene,aw}} = \frac{C_{\text{chrysene,a}}}{C_{\text{chrysene,sewater}}}$

We can write: $C_{\text{chrysene, w}}*V_w = C_{\text{chrysene, a}}*V_a$

And thereofre $V_a = V_w / K_{\text{chrysene,aw}}$.

So we must find $K_{\text{chrysene,aw}}$. First, estimate the K_H for chrysene in seawater, based on the vapor pressure and the solubility in seawater:

$$K_{\text{chrysene, H}} \approx \frac{p^*_{\text{chrysene}}}{C^{\text{sat}}_{\text{chrysene, seawater}}} = 100\ \text{Pa/M} \approx 10^{-3}\text{atm/M}$$

Convert to the $K_{\text{chrysene, aw}}$ in seawater (making sure to use R in the correct units! Here R = 0.082 atm /(M*K)): $K_{\text{chrysene, aw}} = K_{\text{chrysene,H}} / RT \approx 4*10^{-5}$ (L water / L air)

Finally, $V_a = V_w / K_{\text{chrysene,aw}}$ = 25’000 L

7. Chrysene in the golf of Mexico

solutions

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?

First we need to get $K_{chrysene,ow}$ for seawater. From the class notes we know that for an organic compound i, there is a relationship between $K_{i,ow}$ and $C_{i,w}^{sat}$ that has the form:

$\log K_{i,ow,} = -a*\log C_{i,w,}{}^{sat} + b$

Chrysene is a polycyclic aromatic hydrocarbon (PAH). The parameters and b for PAH are a=0.87 and b=0.68.

By inserting $C_{\mathrm{chrysene,\,seawater}}^{\mathrm{sat}}$ into the equation above, we directly obtain the $K_{chrysene,ow}$ for seawater:

$\log K_{chrysene,ow} = -0.87*-8.22+0.68 = 7.83$; $K_{chrysene,ow}$ in seawater = $10^{7.83}$.

Using the same arguments as before we can write

$V_o = V_w / K_{chrysene,ow} = 10^{-7.83}$ L. So the chrysene is efficiently transferred into octanol.

7. Chrysene in the golf of Mexico

solutions

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.

K_{aw} will rapidly increase with increasing temperature, since $\Delta_{vap}H > 0$. The transfer of chrysene from water to air will become more efficient. The larger the K_{aw}, the smaller the volume of air needed.

K_{ow} mainly depends on the aqueous solubility, which is not affected by temperature very much ($\Delta_{wL}H$ is usually close to zero). Therefore changing the temperature would not affect the transfer of chrysene between water and octanol very much.

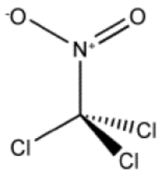
8. Partitioning and decay of chloropicrin

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

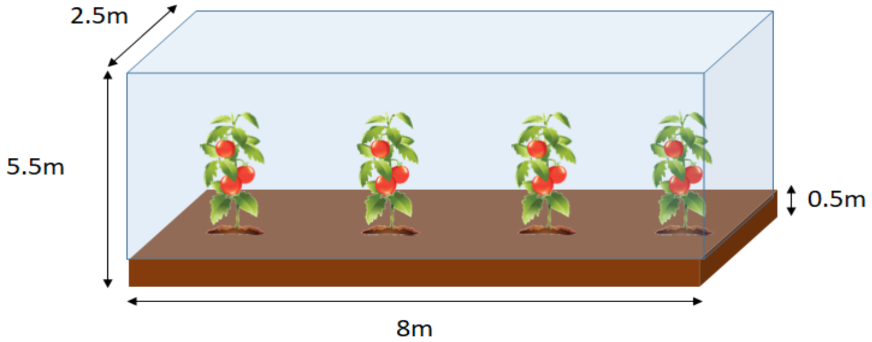
$p_L^* = 0.03$ atm

$K_{ow} = 54$

$K_{tomato\text{-}water} = 7.9$ *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



8. Partitioning and decay of chloropicrin

solutions

a) A farmer would like to grow tomatoes, strawberries and almonds, but she is concerned about the CP content in these plants. The 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).

Neutral organic compounds like CP are typically hydrophobic and like aploar, hydrophobic solvents. They will therefore mainly partition into the lipid fraction of plants. Here, almonds have the highest lipid content, so they will take up the most CP.

8. Partitioning and decay of chloropicrin

solutions

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?

The fraction of CP in the tomato (f_{tomato}) corresponds to:

$$f_{tomato} = \frac{C_{tomato} M_{tomato}}{C_{tomato} M_{tomato} + C_{Soil} M_{soil} + C_{air} V_{air}} = \frac{1}{1 + K_{soil-tomato} \frac{M_{soil}}{M_{tomato}} + \frac{1}{K_{tomato-air}} \frac{V_{air}}{M_{tomato}}}$$

Need to find M_{soil}, V_{air}, $K_{tomato-air}$, and $K_{soil-tomato}$.

M_{soil} can be calculated based on the V_{soil} and the density. First, get V_{soil}, taking into account the porosity of 0.5: V_{soil} = 0.5m * 20m^2 * 0.5 = 5 m^3 = 5000 L. M_{soil} = 5000 L * 2 kg/L = 10’000 kg

To determine V_{air}, we assume that the volume of the tomatoes is insignificant. Then:
V_{air} = V_{total} - V_{soil} = 20m^2*5.5m- 5m^3 = 105 m^3 = 105’000 L

$K_{tomato-air}$ can be calculated from $K_{tomato-water}$ and K_{aw}, where K_{aw},= (p_L^*/C_w^{sat}) / RT = (0.03 atm/0.012 M)/(0.082 L· atm· K^{-1}·mol^{-1} · 298 K) = 0.102.
$K_{tomato-air}$ = $K_{tomato-water}$ /$K_{air-water}$. = 7.9/0.102 = 77.5 L air / kg dry weight

$K_{soil-tomato}$ can be calculated from K_d / $K_{tomato-water}$. $K_{tomato-water}$ is given in the exercise. K_d can be estimated using the K_{ow} and the fraction of organic carbon:
K_d = f_{oc} * K_{oc}, where log K_{oc} = 0.57*log K_{ow} + 0.66 = 1.65. (I used the relationship for C1 and C2 chlorocarbons. The K_{ow} falls in the right range, and CP is a C1 chlorocarbon).
K_d = 0.3*10$^{1.65}$ = 13.4 L/kg
$K_{soil-tomato}$ = K_d / $K_{tomato-water}$ = 13.4/ 7.9 = 1.7 kg dry weight/kg soil

Now we can calculate f_{tomato} = 0.0003.

8. Partitioning and decay of chloropicrin

solutions

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?

Since volatilization and photolysis are parallel processes that proceed at similar rate, we need to account for both of their contributions. This means we need to sum up their rate constants. The half life of each process and the corresponding k are linked by:

$t_{1/2} = \ln 2 / k$

The individual first-order rate constants correspond to:

$k_{volatilization} = \ln 2/4.3 \text{ days} = 0.16 \text{ day}^{-1}$

$k_{photolysis} = \ln 2/3 \text{ days} = 0.23 \text{ day}^{-1}$

The total removal rate constant is: $k_{total} = k_{volatilization} + k_{photolysis} = 0.39 \text{ day}^{-1}$

The time to reach 10% of the initial concentration is:

$C = 0.1 * C_0 = C_0 * e^{-0.39*t}$

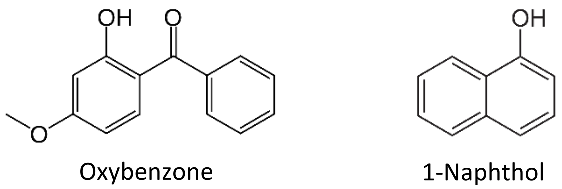
t = 5.9 days

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.



Structures of oxybenzone and 1-naphthol

9. Fate of oxybenzone in sea water

solutions

a. What is the solubility of oxybenzone in seawater?

First calculate the solubility in pure water based on the LFER for $K_{ow,oxybenzone}$ and C_w^{sat} for PAHs:

$\log K_{ow,\ oxybenzone} = -0.87^* \log C_w^{sat} + 0.68$

$\log C_w^{sat} = (3.6-0.68)/-0.87 = -3.36$

$C_w^{sat} = 10^{-3.36}\mathrm{M} = 4.4\ \mathrm{mM}$

Then determine the solubility in seawater using the relationship $C_{i,w,salt}^{sat} = C_{i,w}^{sat} * 10^{-K_i^s[salt]}$

Whereby the salt concentration is 0.5M and K^s of 1-naphthol = 0.23

We find: $C_{w,salt}^{sat}=10^{-3.36}*10^{-0.23*0.5}=10^{-3.475}$ M = **3.3 mM**

9. Fate of oxybenzone in sea water

solutions

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?

Here we need to determine the volume of seawater needed such that f_w = 0.9 and $f_{sunscreen}$=0.1. The fraction in water is (note that I use the subscript “o” for octanol, because sunscreen behaves like octanol):

$$f_w = \frac{1}{1+K_{ow,oxybenzone}\frac{V_o}{V_w}}$$

Or easier, we can simply write: $C_wV_w = 9*C_oV_o \rightarrow V_w = 9* K_{ow,\ oxybenzone} *V_o$

We determine V_o from the mass and density of sunscreen and find:

V_o = 30 g/(1 g/cm^3) = 30 cm^3= 0.03 L

We also need to consider that the $K_{ow,\ oxybenozne}$ here should be $K_{ow,\ oxybenzone,\ salt}$, since we are in seawater. We know that the K_{ow} is mainly determined by the aqueous solubility, therefore if the solubility decreases by a factor X then $K_{ow,\ oxybenzone,\ salt}$ will increase by X. Using the latter approach, we determine $K_{ow,oxybenzone,\ salt}$ as:

$\mathbf{K_{ow,\ oxybenzone,\ salt}} = K_{ow,oxybenzone} * (C_{w,}{}^{sat} / C_{w,salt}{}^{sat})$ = **5188 = $\mathbf{10^{3.715}}$**

Finally, we find:

$\mathbf{V_w} = 9*K_{ow,oxbenzone,\ salt}*V_o = 9*5188*0.03$ = **1400 L**

9. Fate of oxybenzone in sea water

solutions

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.

First, we calculate the total amount (in moles) of oxybenzone that enters the water with each swimmer. We know that each swimmer carries 30 g of sunscreen, which is composed of 0.03 g/g of oxybenzone. So the total mass of oxybenzone per swimmer is 30*0.03 = 0.9 g.

Next, we determine the fraction of oxybenzone that is present in a water volume of 10 m^3.
As stated in exercise b), the fraction in the water is:

$$f_w = \frac{1}{1+K_{ow,oxybenzone,salt}\frac{V_o}{V_w}} = \frac{1}{1+10^{3.715}\frac{0.03\ \text{L}}{10'000\text{L}}} = 0.98$$

So 98% of the total mass is present in the water. This yields a concentration of 0.98*0.9g/10’000L = **88 µg/L**. With only one swimmer, the toxicity level is already far exceeded.