

CHEM 301

Assignment #3

Provide solutions to the following questions in a neat and well organized manner.

Clearly state assumptions and reference sources for any constants used.

Due date: November 18th

1. Methane and carbon dioxide are produced under anaerobic conditions by the fermentation of organic matter, approximated by the following equation



As gas bubbles are evolved at the sediment interface at 5 m depth and remain in contact with water at the sediment surface long enough so that equilibrium is attained. The total pressure at this depth is 148 kPa. If the pH is 8.20, calculate the total carbonate concentration in the interstitial water at 25°C. How would you expect your answer to change if these gas bubbles were present at 500 m depth?

Strategy: The total pressure inside the gas bubble must be equal to the total pressure on the outside of the gas bubble (or else it would either explode or collapse). Furthermore, the total pressure inside that gas bubble is equal to the sum of the partial pressures of CH₄ and CO₂. We can then use the partial pressure of CO₂ inside the gas bubble and the corresponding Henry's law constant to calculate the concentration of aqueous CO₂ at equilibrium. Given the pH of the solution and the expressions for K_{a1} and K_{a2}, we can determine the concentration of HCO₃⁻ and CO₃²⁻. (see textbook pgs 241-242; Chap 11, Q9)

Solution:

The total carbonate concentration is given by;

$$[\text{CO}_3^{2-}]_T = [\text{CO}_2(\text{aq})] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

From the pH speciation diagram (Fig. 1.2 text), we can see that at pH 8.2, the vast majority of the inorganic carbon present is in the form of the bicarbonate ion (i.e., $[\text{HCO}_3^-] \gg [\text{CO}_2(\text{aq})] \approx [\text{CO}_3^{2-}]$).

So we can write,

$$[\text{CO}_3^{2-}]_T \approx [\text{HCO}_3^-]$$

In order to 'solve' this problem, we need find the partial pressure of CO₂, which is in equilibrium with the surrounding water. Since this reaction is occurring under anaerobic conditions, these are the only gases likely to be present at appreciable concentrations and they are produced with 1:1 stoichiometry. Therefore,

$$P_T = 148 \text{ kPa} = P_{\text{CO}_2} + P_{\text{CH}_4}$$

$$\text{and } P_{\text{CO}_2} = P_{\text{CH}_4} = 74 \text{ kPa}$$

To calculate the total carbonate, we will first need the $[\text{CO}_2(\text{aq})]$.

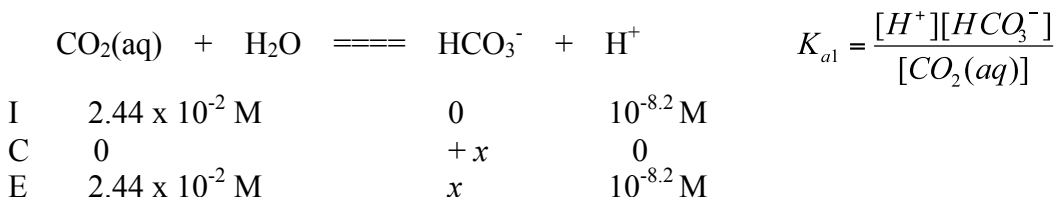
From the Henry's Law expression;

$$[\text{CO}_2(\text{aq})] = K_{\text{H}} P_{\text{CO}_2}$$

Using the K_{H} value in Table 11.1 (textbook) yields;

$$[\text{CO}_2(\text{aq})] = 3.3 \times 10^{-7} \text{ M Pa}^{-1} \times 74,000 \text{ Pa} = 2.44 \times 10^{-2} \text{ M}$$

Using this value in the K_{a1} expression and substituting in the $[\text{H}^+] = 10^{-8.2} \text{ M}$, allows us to calculate the $[\text{HCO}_3^-]$ as follows;



$$\therefore [\text{HCO}_3^-] = \frac{K_{\text{a1}} [\text{CO}_2]}{[\text{H}^+]} = \frac{(4.5 \times 10^{-7})(2.44 \times 10^{-2})}{10^{-8.2}} = 1.75 \text{ M}$$

So, $[\text{CO}_3^{2-}]_{\text{T}} \approx [\text{HCO}_3^-] = 1.75 \text{ M}$

Note: this represents an upper limit, since the assumption is that the supply of CO_2 is inexhaustible (i.e., the change in $[\text{CO}_2(\text{aq})]$ as the acid dissociation reaction proceeds is assumed to be negligible). This is clearly not the case here since the CO_2 in the gas bubble is consumed as the reaction proceeds. In order to correct for this, we would need additional information such as the size of the gas bubble so that we could determine the number of moles of CO_2 molecules present.

At 500 m depth in the water column, the partial pressure inside the gas bubbles would necessarily be much greater and the calculated total carbonate concentration would be huge. Again, this results in an unrealistically high value.

2. Use the following chemical equilibrium for a water sample in equilibrium with atmospheric $\text{CO}_2(\text{g})$ and limestone (CaCO_3). In such a system, the concentrations of H^+ and Ca^{2+} are coupled to each other and to the partial pressure of CO_2 .



Calculate the solubility of CaCO_3 in equilibrium with $P_{\text{CO}_2} = 390 \text{ ppmv}$. What effect will a doubling of the atmospheric concentration of CO_2 have on your result?

Strategy: The solubility of $\text{CaCO}_3(\text{s})$ will be given by the concentration of Ca^{2+} in equilibrium with solid calcium carbonate and an inexhaustible supply of atmospheric carbon dioxide. If we can determine the value of the equilibrium constant for the above reaction and independently determine the concentration of HCO_3^- , we can rearrange the expression and calculate the $[\text{Ca}^{2+}]$. Alternatively, we can write the solubility product expression for CaCO_3 and rearrange for $[\text{Ca}^{2+}]$. Making the appropriate substitutions, we can derive an expression for $[\text{Ca}^{2+}]$ in terms of a series of equilibrium constants and the $[\text{H}^+]$. Since we have two variables and two unknowns, we use a second independent expression (i.e., charge balance) to solve for both $[\text{H}^+]$ and $[\text{Ca}^{2+}]$. (see textbook pgs 242-244)

Solution:

The solubility of calcium carbonate and thus the concentration of Ca^{2+} , will vary with changes in the P_{CO_2} and $[\text{H}^+]$. To derive an expression for the $[\text{Ca}^{2+}]$ as a function of P_{CO_2} , we must first determine the $[\text{H}^+]$.

Rearranging the K_{sp} expression for CaCO_3 , we can write;

$$[\text{Ca}^{2+}] = K_{\text{sp}}/[\text{CO}_3^{2-}]$$

Remembering that we wish to express the $[\text{Ca}^{2+}]$ in terms of P_{CO_2} and $[\text{H}^+]$, we look for an appropriate substitution for $[\text{CO}_3^{2-}]$.

Rearranging the $K_{\text{a}2}$ expression gives;

$$[\text{CO}_3^{2-}] = K_{\text{a}2} [\text{HCO}_3^-]/[\text{H}^+]$$

and we can substitute for $[\text{HCO}_3^-]$ using the $K_{\text{a}1}$ expression;

$$[\text{HCO}_3^-] = \{K_{\text{a}1}[\text{CO}_2(\text{aq})]/[\text{H}^+]\}$$

and we can substitute for $[\text{CO}_2(\text{aq})]$ using the K_{H} expression;

$$[\text{CO}_2(\text{aq})] = K_{\text{H}} P_{\text{CO}_2}$$

Making these substitutions into the expression for $[\text{Ca}^{2+}]$ gives;

$$[Ca^{2+}] = \frac{K_{sp}[H^+]^2}{K_{a1}K_{a2}K_H P_{CO2}}$$

From this expression we can see that the concentration of calcium depends not only on the P_{CO2} , but also on the equilibrium concentration of $[H^+]$ – which we know will also depend on the P_{CO2} .

To derive an expression for the $[H^+]$ as a function of P_{CO2} , we will need an additional independent relationship – the charge balance equation. Since all solutions are electrically neutral, we can write that the sum total of positive charges is equal to the sum total of negative charges.

Thus;

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

For most natural water in contact with solid $CaCO_3$ (pH ranges 5-9), this simplifies to;

$$2 [Ca^{2+}] = [HCO_3^-]$$

$$\begin{aligned} &\text{since } [Ca^{2+}] \gg [H^+] \\ &\text{and} \\ &[HCO_3^-] \gg [CO_3^{2-}] \text{ and } [OH^-] \end{aligned}$$

So from the charge balance, we can write; $[Ca^{2+}] = \frac{1}{2} [HCO_3^-]$

Using the K_{a1} and K_H expressions to substitute for the $[HCO_3^-]$ in terms of $[H^+]$ and P_{CO2} (as before), yields;

$$[Ca^{2+}] = \frac{K_{a1}K_H P_{CO2}}{2[H^+]}$$

Since we now have two expressions for the concentration of Ca^{2+} (one derived from the K_{sp} expression and the other from the charge balance), we can set them equal to each other and solve for $[H^+]$ as a function of only the P_{CO2} .

Thus;

$$\frac{K_{sp}[H^+]^2}{K_{a1}K_{a2}K_H P_{CO2}} = \frac{K_{a1}K_H P_{CO2}}{2[H^+]}$$

Rearranging and solving for $[H^+]$ yields;

$$[H^+] = \sqrt[3]{\frac{K_{a1}^2 K_H^2 K_{a2} P_{CO2}^2}{2K_{sp}}}$$

Thus, we have an expression to calculate the $[H^+]$ at any P_{CO2} . We can use this and then substitute both the $[H^+]$ and the P_{CO2} into the expression for $[Ca^{2+}]$ above and calculate the equilibrium concentration of calcium.

$$[H^+] = \sqrt[3]{\frac{K_{a1}^2 K_H^2 K_{a2} P_{CO2}^2}{2K_{sp}}} = \sqrt[3]{\frac{(4.5 \times 10^{-7} M)^2 (3.3 \times 10^{-7} \text{ MPa}^{-1})^2 (4.7 \times 10^{-11} M) (39.5 \text{ Pa})^2}{2 (5 \times 10^{-9} M^2)}}$$

$$= 5.45 \times 10^{-9} M \text{ (i.e., pH} = 8.26)$$

$$[Ca^{2+}] = \frac{K_{sp} [H^+]^2}{K_{a1} K_{a2} K_H P_{CO2}} = \frac{(5 \times 10^{-9} M^2) (5.45 \times 10^{-9} M)^2}{(4.5 \times 10^{-7} M) (4.7 \times 10^{-11} M) (3.3 \times 10^{-7} M \text{ Pa}^{-1}) (39.5 \text{ Pa})}$$

$$\therefore [Ca^{2+}] = 5.39 \times 10^{-4} M$$

In other words, 0.54 millimoles of $CaCO_3(s)$ dissolves in 1 L of water in equilibrium with atmospheric CO_2 at 390 ppmv.

Doubling of the P_{CO2} from 390 ppmv to 780 ppmv yields the following;

$$[H^+] = 8.65 \times 10^{-9} M \text{ (i.e., pH} = 8.06)$$

and

$$[Ca^{2+}] = 6.78 \times 10^{-4} M$$

In other words, the solubility of $CaCO_3$ increases by 25% if P_{CO2} doubles.

Note: For gases, a ppm is defined as a volume ratio (hence ppmv) and since the partial pressure of a gas is directly proportional to it's partial volume (via $P = nRT/V$), we can write;

$$P_{CO2} = (390 \times 10^{-6}) P_T, \text{ where } P_T \text{ at sea-level is } 101,300 \text{ Pa}$$

$$\text{Hence, } P_{CO2} @ 390 \text{ ppmv} = 39.5 \text{ Pa}$$

3. Sulfur dioxide is soluble in water, $K_H = 1.8 \times 10^{-5} \text{ mol L}^{-1} \text{ Pa}^{-1}$ at 25°C. Calculate the equilibrium aqueous concentration of SO_2 in raindrops, if the air contains 2.0 ppmv of $\text{SO}_2(\text{g})$. Calculate the pH of this rain. How would your answer change if the dissolved sulfur dioxide is oxidized to sulfur trioxide? Justify your answer.

Strategy: The concentration of aqueous SO_2 in equilibrium with an inexhaustible supply of atmospheric $\text{SO}_2(\text{g})$ will be given by the partial pressure of sulfur dioxide and the value of the corresponding Henry's law constant. To calculate the pH of the solution, we will need the value of the acidic dissociation constant for sulfurous acid. (see textbook pgs 241-242; Chap 11 Q6)

Solution:

We will need to consider both the dissolution of $\text{SO}_2(\text{g})$ into water (K_H) and the subsequent dissociation to produce protons (K_{a1} and K_{a2}). These equilibria are summarized below.



Assuming a total pressure of one atmosphere, the $P_{\text{SO}_2} = 2.0 \times 10^{-6} \text{ atm}$.

Converting the given K_H into atmospheres yields;

$$1.8 \times 10^{-5} \text{ M Pa}^{-1} \times 101,300 \text{ Pa atm}^{-1} = 1.82 \text{ M atm}^{-1}$$

$$\text{Thus, } [\text{SO}_2(\text{aq})] = K_H \times P_{\text{SO}_2} = (1.82 \text{ M atm}^{-1}) (2.0 \times 10^{-6} \text{ atm}) = 3.64 \times 10^{-6} \text{ M}$$

Using the K_{a1} expression and assuming no further dissociation of HSO_3^- (i.e., ignoring K_{a2}), yields;

$$K_{a1} = \frac{x^2}{[\text{SO}_2(\text{aq})]},$$

where $x = [\text{H}^+] = [\text{HSO}_3^-]$ and we assume that the atmosphere provides an inexhaustible supply of $\text{SO}_2(\text{aq})$

$$\therefore [\text{H}^+]^2 = (1.72 \times 10^{-2}) (3.64 \times 10^{-6})$$

so

$$[\text{H}^+] = 2.50 \times 10^{-4} \text{ M}$$

$$\therefore \text{pH} = 3.60$$

If the $\text{SO}_2(\text{aq})$ is oxidized to $\text{SO}_3(\text{aq})$, the pH will be even lower since the resulting sulfuric acid (H_2SO_4) is stronger than sulfurous acid (H_2SO_3). See further the K_{a1} and K_{a2} values for H_2SO_4 .

Note 1: A much lower pH results from a smaller amount of SO₂ than for CO₂. This is the result of two factors $K_H(\text{SO}_2)$ is larger and $K_{a1}(\text{SO}_2)$ is larger.

Note 2: If we consider the second dissociation using the K_{a2} expression, we solve for an additional $[\text{H}^+] = (K_{a2} \times [\text{HSO}_3^-])^{1/2} = 3.6 \times 10^{-6} \text{ M}$, which makes a relatively insignificant contribution to the pH when added to the $3.05 \times 10^{-4} \text{ M}$ already present from the first dissociation, $[\text{H}^+] \sim 2.05 \times 10^{-4} + 3.6 \times 10^{-6} = 2.09 \times 10^{-4} \text{ M}$, so pH = 3.68.

4. Estimate the fraction of lead complexed to fulvic acid in a sample containing 3.6 µg/L of lead and 12 mg/L of DOM (as fulvic acid) at pH 5. Assume a $[FA_{CO_2-}] = 4.5 \text{ mmol g}^{-1}$ of DOM and that lead is the only metal ion in solution. $K_f(Pb^{2+}-FA) = 1.1 \times 10^4$

Strategy: The fraction of lead complexed to FA relative to the total amount of lead can be determined if we calculate the concentration of lead complexed to FA. We approach this by writing the chemical equilibrium for the complexation of lead by FA and the corresponding formation constant expression (K_f). Distinguishing between 'free' and 'complexed' forms of both Pb and FA_{CO_2-} , allows us to complete this calculation.
(see textbook pgs 265-266, 283-286, Chap 13 Q5)

Solution:

This question requires some knowledge of the association constant (K_f') between Pb^{2+} and fulvic acid, given in Table 13.3 in your textbook and some assumption about the average concentration of carboxylate groups ($C_{CO_2-} \sim 4.5 \text{ mmol/g}$) given in the question.

We need to calculate the fraction of lead bound to FA, which we can define as follows;

$$\text{Fraction Pb-FA} = \frac{[Pb-FA_{CO_2-}]}{[Pb]_T}$$

where $[Pb-FA_{CO_2-}]$ represents the concentration of lead complexed to fulvics and $[FA_{CO_2-}]_T$ represents the total concentration of fulvic acid carboxylates. We will further define the following terms; $[Pb^{2+}]_T$, $[Pb^{2+}]_{\text{free}}$ and $[FA_{CO_2-}]_{\text{free}}$

Such that

$$[Pb^{2+}]_T = [Pb^{2+}]_{\text{free}} + [Pb-FA_{CO_2-}]$$

and

$$[FA_{CO_2-}]_T = [FA_{CO_2-}]_{\text{free}} + [Pb-FA_{CO_2-}]$$

From the information provided in the question;

$$[Pb^{2+}]_T = 3.6 \times 10^{-6} \text{ g/L} \times 1 \text{ mol}/207.2 \text{ g} = 1.74 \times 10^{-8} \text{ M}$$

$$[FA_{CO_2-}]_T = (12 \times 10^{-3} \text{ g/L}) \times (4.5 \times 10^{-3} \text{ mol/g}) = 5.4 \times 10^{-5} \text{ M}$$

Since $[Pb^{2+}]_T \ll [FA_{CO_2-}]_T$

$$[FA_{CO_2-}]_T \sim [FA_{CO_2-}]_{\text{free}}$$

(i.e., the vast majority of FA_{CO_2-} is not complexed to Pb)

The relevant reaction is given by;



$$1.1 \times 10^4 = \frac{[\text{Pb} - \text{FA}_{\text{CO}_2}^-]}{[\text{Pb}^{2+}]_{\text{free}} [\text{FA}_{\text{CO}_2}^-]_{\text{free}}}$$

If we let x represent the concentration of complexed fulvic acid ($[\text{Pb} - \text{FA}_{\text{CO}_2}^-]$), then

$$[\text{Pb}^{2+}]_{\text{free}} = 1.74 \times 10^{-8} \text{ M} - x$$

Further, we can assume that the $[\text{FA}_{\text{CO}_2}^-]_{\text{free}} \sim [\text{FA}_{\text{CO}_2}^-]_{\text{T}} = 5.4 \times 10^{-5} \text{ M}$

so

$$1.1 \times 10^4 = \frac{x}{(1.74 \times 10^{-8} - x)(5.4 \times 10^{-5} \text{ M})}$$

$$x = (5.4 \times 10^{-5}) (1.74 \times 10^{-8} - x) (1.1 \times 10^4) = 1.034 \times 10^{-8} - 0.594 x$$

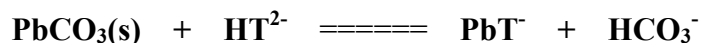
$$\text{and } 1.594 x = 1.034 \times 10^{-8}$$

$$\text{so } x = 6.487 \times 10^{-9} \text{ M} = [\text{Pb} - \text{FA}_{\text{CO}_2}^-]$$

$$\text{Therefore the fraction of lead complexed} = (6.49 \times 10^{-9} / 1.74 \times 10^{-8}) = 0.373$$

In other words, under the stated conditions, roughly 37% of the lead is bound to fulvic acid.

5. What fraction of NTA is uncomplexed after H_2T^- has been brought to equilibrium with solid PbCO_3 at pH 7 in aqueous solution with $[\text{HCO}_3^-] = 1.25 \times 10^{-3} \text{ M}$.

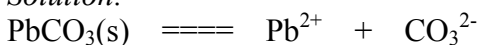


$$\log K_{\text{sp}}(\text{PbCO}_3) = -13.13$$

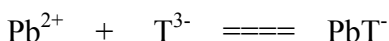
$$\log K_{\text{f}}(\text{PbT}^-) = 11.34$$

Strategy: We want to solve for the fraction of free NTA to the total NTA in solution, which will include some NTA complexed to Pb^{2+} ions. Since at pH 7, the predominant form of NTA is HT^{2-} , this fraction we are interested in is $[\text{HT}^{2-}]/([\text{HT}^{2-}] + [\text{PbT}^-])$. To solve this, we will write out the expression for the equilibrium above and rearrange to isolate $[\text{PbT}^-]$. (see textbook pgs 293-296, Chap 13 Q4)

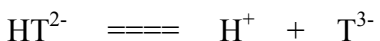
Solution:



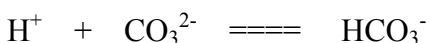
$$K_{\text{sp}} = 10^{-13.13} = 7.41 \times 10^{-14}$$



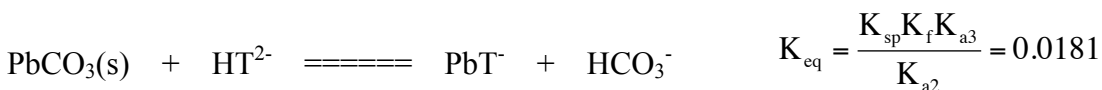
$$K_{\text{f}} = 10^{11.34} = 2.19 \times 10^{11}$$



$$K_{\text{a3}} = 10^{-10.28} = 5.25 \times 10^{-11} \text{ (pg 294)}$$



$$K_{\text{a2}}^{-1} = (4.7 \times 10^{-11})^{-1} = 2.13 \times 10^{10}$$



Since,

$$K_{\text{eq}} = \frac{[\text{PbT}^-] [\text{HCO}_3^-]}{[\text{HT}^{2-}]}$$

$$\text{rearranging for } [\text{PbT}^-] = \frac{K_{\text{eq}} [\text{HT}^{2-}]}{[\text{HCO}_3^-]}$$

and substituting into the fractional abundance expression;

$$\alpha_{\text{HT}^{2-}(\text{free})} = \frac{[\text{HT}^{2-}]}{[\text{HT}^{2-}] + [\text{PbT}^-]} = \frac{[\text{HT}^{2-}]}{[\text{HT}^{2-}] + \frac{K_{\text{eq}} [\text{HT}^{2-}]}{[\text{HCO}_3^-]}} = \frac{1}{1 + \frac{K_{\text{eq}}}{[\text{HCO}_3^-]}}$$

Substituting in for the value of K_{eq} (above) and the concentration of bicarbonate ion given in the question, yields;

Fraction of free NTA = 0.0645 (or ~ 6.5%)

6. In the “Times Beach” incident, a waste oil hauler removed 18,500 US gallons of oil contaminated by 33 ppm of ‘dioxin’ from a 2,4,5-T manufacturing plant.
- What mass of dioxin was involved? (assume the oil density is $\sim 1 \text{ g/mL}$)
 - Some horse arenas that were sprayed with this waste oil had solid matter concentrations of 1750 ppb ($\mu\text{g/kg}$). What mass of this solid matter needs to be ingested by a 25 g mouse to reach the LD_{50} of 114 μg per kg?

Strategy: We know the concentration of ‘dioxin’ as a mass ratio (i.e., $\text{ppm} = \text{mg/kg}$) and we can convert the volume of oil to a corresponding mass, therefore the total mass of ‘dioxin’ can be determined.

For the second part, we scale the LD_{50} given as μg per kg to the mass of a mouse and determine the mass of solid matter that contains an equivalent mass of ‘dioxin’.

Solution:

- Mass of dioxin involved =

$$\frac{33 \text{ mg}}{\text{kg}} \times \frac{18,500 \text{ US gallons}}{1 \text{ USgallon}} \times \frac{3.78 \text{ L}}{1 \text{ L}} \times \frac{1 \text{ kg}}{1 \text{ L}} \times \frac{1 \text{ g}}{10^3 \text{ mg}} \times \frac{1 \text{ kg}}{10^3 \text{ g}} = 2.3 \text{ kg}$$

- Mass of dioxin to reach LD_{50} in 25 g mouse = $114 \mu\text{g/kg} \times 0.025 \text{ kg} = 2.85 \mu\text{g}$.

Mass of contaminated solid matter containing 1750 $\mu\text{g/kg}$ =

$$2.85 \mu\text{g} \times \frac{1 \text{ kg}}{1750 \mu\text{g}} = 1.63 \times 10^{-3} \text{ kg (or 1.6 g of contaminated solid matter)}$$

7. Report the octanol-water partition coefficients and bioconcentration factors for the pesticides hexachlorocyclohexane (HCH) and isopropyl N-phenylcarbamate (IPA). Draw their structures and illustrate how they may associate with dissolved organic matter in aqueous solution. Suggest where these compounds will distribute in the environment on a triangular air-soil-water distribution plot.

Strategy:

(see further textbook pgs 267-269 and Chap 20; various websites including,

<http://www.srcinc.com/what-we-do/databaseforms.aspx?id=381>

and

<http://logkow.cisti.nrc.ca/logkow/index.jsp>)

Physical and biological properties;

hexachlorocyclohexane – gamma isomer (CAS# 58-89-9)

Log Kow = 3.55; log BCF = 3.10 (fish)

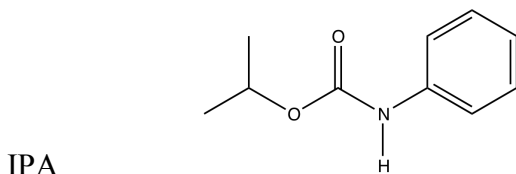
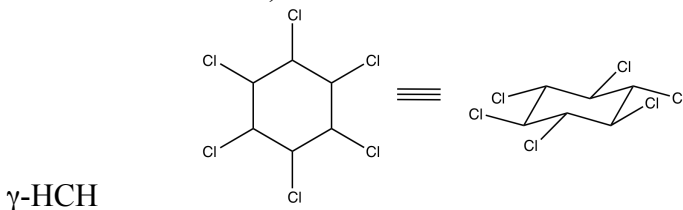
S. Noegrohati and W.E. Hammers, "Regression models for octanol-water partition coefficients and for bioconcentration in fish", [Toxicol. Environ. Chem.](#) 34(2-4), 155-173 (1992).

Isopropyl N-phenylcarbamate (CAS# 122-42-9)

Log Kow = 2.60; log BCF 1.43 (species not specified)

G.G. Briggs, "Theoretical and experimental relationships between soil adsorption, octanol-water partition coefficients, water solubilities, bioconcentration factors and the parachor", [J. Agric. Food Chem.](#) 29(5), 1050-1059 (1981).

Chemical Structures;



Types of humic interactions possible;

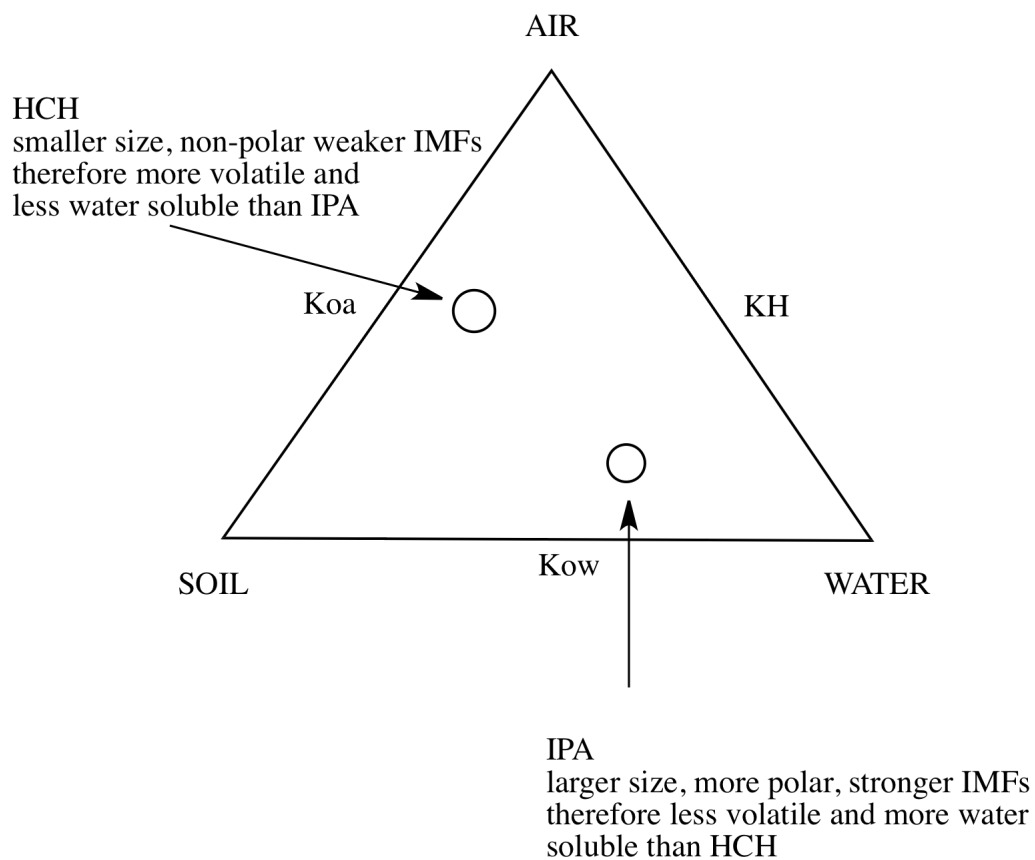
HCH (see Fig 12.7, text)

Non-polar contaminant will have affinity for hydrophobic portions of humate.

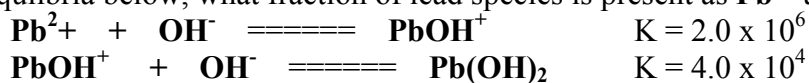
IPA (see Fig 12.5, text)

Carbamates can act as both H-bonding acceptors on the oxygens and H-bonding donors on the N-H group.

Environmental distributions;



8. Given the equilibria below, what fraction of lead species is present as Pb^{2+} at pH 7.



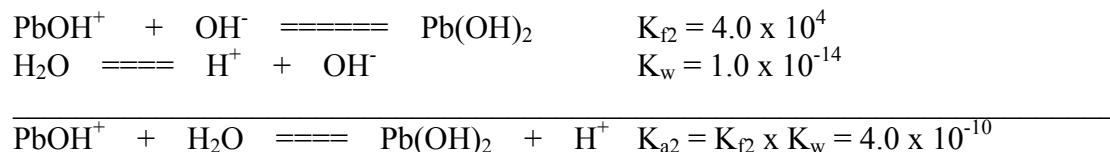
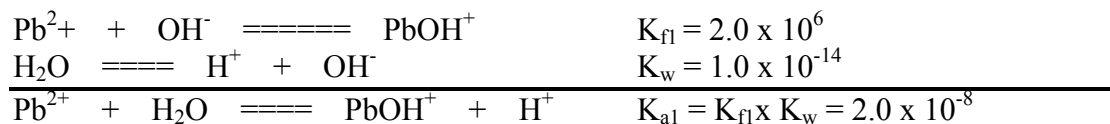
Strategy:

We will need an expression for the fractional abundance of Pb^{2+} as a function of pH. We can approach this in several ways, but to will consistent with out previous discussions on pH speciation, I will re-write these complex ion formations as ‘acid dissociations’.
(see textbook pgs 276-278, Chap 13 Q2)

Solution:

$$\alpha_{\text{Pb}^{2+}} = \frac{[\text{Pb}^{2+}]}{[\text{Pb}^{2+}] + [\text{PbOH}^+] + [\text{Pb(OH)}_2]}$$

Converting given equilibria to acid dissociations by adding the auto-ionization of water yields;



Therefore, $\text{p}K_{a1} = 7.7$ and $\text{p}K_{a2} = 9.4$

Given the magnitude of the $\text{p}K_a$ values, it is reasonable to assume that the concentration of Pb(OH)_2 will be negligible at pH 7, hence we can simplify the fractional abundance expression as;

$$\alpha_{\text{Pb}^{2+}} \approx \frac{[\text{Pb}^{2+}]}{[\text{Pb}^{2+}] + [\text{PbOH}^+]}$$

Rearranging the K_{a1} expression for $[\text{PbOH}^+] = (K_{a1} [\text{Pb}^{2+}]) / [\text{H}^+]$ and substituting into the fractional abundance expression yields;

$$\alpha_{\text{Pb}^{2+}} \approx \frac{[\text{Pb}^{2+}]}{[\text{Pb}^{2+}] + [\text{PbOH}^+]} = \frac{[\text{Pb}^{2+}]}{[\text{Pb}^{2+}] + \frac{K_{a1}[\text{Pb}^{2+}]}{[\text{H}^+]}} = \frac{1}{1 + \frac{K_{a1}}{[\text{H}^+]}} = \frac{[\text{H}^+]}{[\text{H}^+] + K_{a1}}$$

Hence at pH = 7, the fractional abundance of $\text{Pb}^{2+} = 0.833$