

CHEM 301 Assignment #3

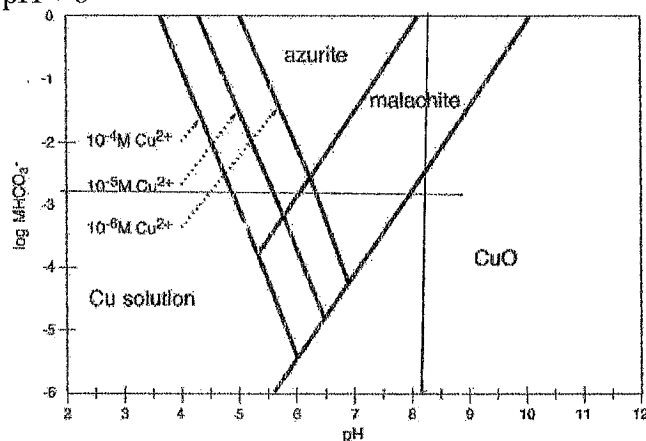
*Provide solutions to the following questions in a neat and organized manner.
Clearly state assumptions and reference sources for any constants used.*

Due date: November 15th.

Only even numbered questions will be assessed.

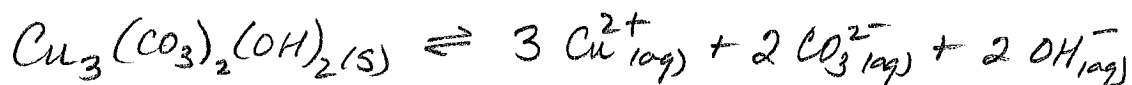
1. The diagram below depicts the dominant chemical speciation for Cu(II) as a function of $\log [\text{HCO}_3^-]$ (M) and pH. Note: 'azurite' = $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ (s) and 'malachite' = $\text{Cu}_2\text{CO}_3(\text{OH})_2$ (s).

- Predict the dominant form of Cu(II) in seawater.
- Explain why the Cu^{2+} /azurite boundary depends on the copper ion concentration.
- Derive an expression for the $\log [\text{HCO}_3^-]$ as a function of pH in the form of $\log [\text{HCO}_3^-] = m \text{pH} + b$



- a) In seawater pH is buffered at $\text{pH} \sim 8.2$ and the bicarbonate ion concentration is roughly 2 mM range. Therefore, at $\text{pH} \sim 8$, $\log [\text{HCO}_3^-] \sim -3$, we have $\text{CuO}(s)$ as the dominate form. Since we are close to the 'malachite' boundary, we might expect some $\text{Cu}_2\text{CO}_3(\text{OH})_2(s)$ present as well.

b) the Cu^{2+} /azurite boundary involves the dissolution/precipitation reaction below.



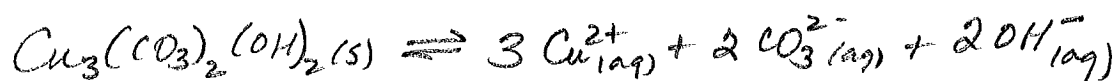
Since Cu^{2+} ion is involved in this equilibrium, we expect that the boundary will depend on $[\text{Cu}^{2+}]$. For example, at higher $[\text{Cu}^{2+}]$, we expect the equilibrium to shift to LEFT and azurite will become less soluble (all else being equal). This is known as the 'common ion' effect described in first yr. chem.

c) Since the figure depicts $\log [\text{HCO}_3^-]$ on the y-axis and pH on the x-axis, we are deriving the equation for the line

$$y = mx + b \quad \text{where } y = \log [\text{HCO}_3^-] \text{ and } x = \text{pH}.$$

To tackle this, we need to identify the chemical process occurring at the boundary.

Using the solubility of azurite for the azurite/ Cu^{2+} boundary, we have;



Therefore, the expression is given by

$K_{sp} = [Cu^{2+}]^3 [CO_3^{2-}]^2 [OH^-]^2$ and it is apparent that the solubility will depend on conc. of Cu^{2+} , CO_3^{2-} and OH^- . So in addition to the $[Cu^{2+}]$, the solubility boundary for azurite depends on the alkalinity (ie. CO_3^{2-} & HCO_3^-) as well as the pH (ie. OH^- & H^+).

Taking log of both sides of the K_{sp} expression yields, $\log K_{sp} = 3 \log [Cu^{2+}] + 2 \log [CO_3^{2-}] + 2 \log [OH^-]$

Since we want an expression in terms of $\log [HCO_3^-]$ and $\log [H^+]$, we need to make some substitutions.

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad \therefore [CO_3^{2-}] = \frac{K_{a2} [HCO_3^-]}{[H^+]}$$

$$\text{and } K_w = [OH^-][H^+] \quad \therefore [OH^-] = \frac{K_w}{[H^+]}$$

$$\text{So } \log K_{sp} = 3 \log [Cu^{2+}] + 2 \log \left(\frac{K_{a2} [HCO_3^-]}{[H^+]} \right) + 2 \log \left(\frac{K_w}{[H^+]} \right)$$

Separating terms gives,

$$\log K_{sp} = 3 \log [Cu^{2+}] + 2 \log K_{a2} + 2 \log [HCO_3^-] + 2 \log \frac{1}{[H^+]} \\ + 2 \log K_w + 2 \log \frac{1}{[H^+]}$$

collecting constant and like terms gives,

$$\underbrace{\log K_{sp} - 3 \log [Cu^{2+}] - 2 \log K_{a2} - 2 \log K_w}_{\text{constant at given } Cu^{2+} \text{ conc.}} = 2 \log [HCO_3^-] + 4 \log \frac{1}{[H^+]}$$

isolating $\log [HCO_3^-]$ yields,

$$\log [HCO_3^-] = -2 \text{ pH} + \underbrace{\frac{1}{2} \log K_{sp} - \frac{3}{2} \log [Cu^{2+}] - \log K_{a2} - \log K_w}_b$$

\uparrow \uparrow \uparrow \uparrow
y m x b

slope, $m = -2$

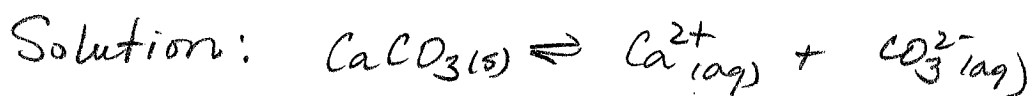
y-intercept, $b = \frac{1}{2} \log K_{sp} - \frac{3}{2} \log [Cu^{2+}] - \log K_{a2} - \log K_w$

since K_{a2} and K_w are known and $[Cu^{2+}]$ can be chosen as $10^{-4} M$, we can write

$$b = \frac{1}{2} \log K_{sp} - \frac{3}{2} (-4) - \log (4.7 \times 10^{-11}) - \log (1.0 \times 10^{-14}) \\ = \frac{1}{2} \log K_{sp} + 6.0 + 10.3 + 14.0 \\ = \frac{1}{2} \log K_{sp} + 30.3$$

2. A water sample has calcium hardness of 65.0 ppm CaCO_3 and a total alkalinity of 120. ppm CaCO_3 . Calculate the pH at which the sample is saturated with respect to calcite ($K_{sp(\text{calcite})} = 3.36 \times 10^{-9}$).

strategy: Use the equilibrium that controls the solubility of calcite to determine the concentration of carbonate ion at given calcium concentration. We can use this and information about HCO_3^- conc. to determine $[\text{H}^+]$ from K_{a2} expression.



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

$$\begin{aligned} [\text{Ca}^{2+}] &= 65.0 \frac{\text{mg CaCO}_3}{\text{L}} \times \frac{1 \text{ mol CaCO}_3}{100.0 \text{ g}} \times \frac{1 \text{ g}}{10^3 \text{ mg}} \times \frac{1 \text{ mol Ca}^{2+}}{1 \text{ mol CaCO}_3} \\ &= 6.50 \times 10^{-4} \text{ mol/L} \end{aligned}$$

$$\begin{aligned} [\text{alk}]_T &= 120. \frac{\text{mg CaCO}_3}{\text{L}} \times \frac{1 \text{ mol CaCO}_3}{100.0 \text{ g}} \times \frac{1 \text{ g}}{10^3 \text{ mg}} \times \frac{2 \text{ mol H}^+}{1 \text{ mol CaCO}_3} \\ &= 2.40 \times 10^{-3} \frac{\text{mol H}^+}{\text{L}} \end{aligned}$$

Since $[\text{alk}]_T = \sum [\text{bases}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-]$

we may need some simplifying assumptions.

Assume $[\text{HCO}_3^-] \gg [\text{CO}_3^{2-}]$ and $[\text{OH}^-]$ (true for vast majority of natural waters)

then $[\text{alk}]_T \approx [\text{HCO}_3^-] = 2.40 \times 10^{-3} \text{ M}$



and $[\text{CO}_3^{2-}] = \frac{K_{sp}}{[\text{Ca}^{2+}]} = \frac{3.36 \times 10^{-9}}{6.50 \times 10^{-4}} = 5.17 \times 10^{-6} \text{ M}$

So $K_{a2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 4.7 \times 10^{-11}$

and $[\text{H}^+] = \frac{K_{a2} [\text{HCO}_3^-]}{[\text{CO}_3^{2-}]}$

Using $[\text{CO}_3^{2-}]$ and $[\text{HCO}_3^-]$ from above
we get,

$$\begin{aligned} [\text{H}^+] &= \frac{(4.7 \times 10^{-11})(2.40 \times 10^{-3})}{(5.17 \times 10^{-6})} \\ &= 2.18 \times 10^{-8} \text{ M} \end{aligned}$$

$\therefore \text{pH} = 7.66$

checking our earlier assumptions, we find that
 $[\text{HCO}_3^-] \gg [\text{CO}_3^{2-}]$ and $[\text{OH}^-]$ at this pH.

3. The effect of increasing atmospheric concentrations on the aqueous solubility of calcite and aragonite forms of calcium carbonate have significant environmental consequence. The saturation index is defined as the ratio of the actual solubility product activities over those at equilibrium as follows.

$$\Omega = Q_{sp}/K_{sp}$$

- What does it mean if $\Omega < 1$?
- Which mineral form calcite or aragonite is more susceptible to aqueous dissolution and why?
- Use the formulas derived in class for the $\text{CO}_2\text{-CaCO}_3\text{-H}_2\text{O}$ system (or the *PHREEQC* program described on pg261 of your textbook) to calculate the solubility of CaCO_3 at pre-industrial CO_2 levels of 280 ppm_v versus present day levels of 400 ppm_v.

- When the saturation index (Ω) is less than unity the product of the ion concentrations is less than their equilibrium concentrations (ie, K_{sp}). Under these conditions, the dissolution of $\text{CaCO}_3(s)$ is spontaneous
- Calcite is less soluble in water than aragonite as seen by their respective solubility products

$$K_{sp}(\text{Calcite}) = 3.31 \times 10^{-9} \quad K_{sp}(\text{Aragonite}) = 4.61 \times 10^{-9}$$

(textbook pg 270 Problem 19)

Calcite and aragonite are polymorphs (different mineral forms with the same empirical formula). Aragonite forms naturally mollusk shells and calcareous endoskeletons of corals. Some organisms have an outer shell dominated by the less soluble calcite form.

Part c)

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 reaction below 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 the question has us calculate the solubility at pre-industrial and current CO_2 concentrations of 280 and 400 ppm_v and the solubility depends on both the P_{CO_2} and the pH, we will need to take both factors into account.



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;

$$[\text{Ca}^{2+}] = \frac{K_{\text{sp}} [\text{H}^+]^2}{K_{\text{a}1} K_{\text{a}2} K_{\text{H}} P_{\text{CO}_2}}$$

From this expression, we can see that the concentration of calcium depends not only on the P_{CO_2} , but also on the equilibrium concentration of $[\text{H}^+]$ – which we know will also depend on the P_{CO_2} .

To derive an expression for the $[H^+]$ as a function of P_{CO_2} , 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;

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

Since, $[Ca^{2+}] \gg [H^+]$

and

$[HCO_3^-] \gg [CO_3^{2-}]$ and $[OH^-]$

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_{CO_2} (as before), yields;

$$[Ca^{2+}] = \frac{K_{a1} K_H P_{CO_2}}{2[H^+]}$$

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_{CO_2} .

Thus;

$$\frac{K_{sp} [H^+]^2}{K_{a1} K_{a2} K_H P_{CO_2}} = \frac{K_{a1} K_H P_{CO_2}}{2[H^+]}$$

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

$$[H^+] = \sqrt[3]{\frac{K_{a1}^2 K_H^2 K_{a2} P_{CO_2}^2}{2K_{sp}}}$$

Thus, we have an expression to calculate the $[H^+]$ at any P_{CO_2} . We can use this and then substitute both the $[H^+]$ and the P_{CO_2} into the expression for $[Ca^{2+}]$ above and calculate the equilibrium concentration of calcium.

Using the K_{sp} for aragonite (4.61×10^{-9}) and K_H for CO_2 ($3.3 \times 10^{-7} \text{ M Pa}^{-1}$) at $P_{\text{CO}_2} = 28.3 \text{ Pa}$ (280 ppm_v).

$$[H^+] = \sqrt[3]{\frac{K_{a1}^2 K_H^2 K_{a2} P_{\text{CO}_2}^2}{2K_{sp}}} = \sqrt[3]{\frac{(4.5 \times 10^{-7})^2 (3.3 \times 10^{-7})^2 (4.7 \times 10^{-11}) (28.3)^2}{2(4.61 \times 10^{-9})}}$$

$$= 4.48 \times 10^{-9} \text{ M (pH} = 8.35)$$

and

$$[Ca^{2+}] = \frac{K_{sp} [H^+]^2}{K_{a1} K_{a2} K_H P_{\text{CO}_2}} = \frac{(4.61 \times 10^{-9})(4.48 \times 10^{-9})^2}{(4.5 \times 10^{-7})(4.7 \times 10^{-11})(3.3 \times 10^{-7})(28.3)} = 4.69 \times 10^{-4} \text{ M}$$

Repeating this calculation at $P_{\text{CO}_2} = 40.5 \text{ Pa}$ (400 ppm_v), we get

$$[H^+] = 5.69 \times 10^{-9} \text{ M (pH} = 8.24)$$

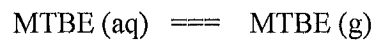
and

$$[Ca^{2+}] = 5.27 \times 10^{-4} \text{ M}$$

Thus, the solubility of aragonite has increased by $(5.27 - 4.69) / (4.69) = 0.124$ (12.4%) on increasing the atmospheric CO_2 concentration.

4. Methyl-*t*-butyl ether (MTBE) is a common gasoline additive used to improve the combustion characteristics. Careless use over the years has resulted in groundwater contamination. Using a reported value for K_H of MTBE of $5.8 \times 10^{-4} \text{ atm m}^3 \text{ mol}^{-1}$, calculate the partial pressure of MTBE in adjacent air-filled pores in the soil if the groundwater contains 175 ppm of MTBE.

Strategy: We note that the units given for K_H are pressure (atm) times inverse concentration (m^3/mol). Therefore, the K_H given is for the equilibrium of aqueous MTBE into the gas phase as written here;



$$K_H = \frac{P_{\text{MTBE}}}{[\text{MTBE}]} = 5.8 \times 10^{-4} \frac{\text{atm m}^3}{\text{mol}}$$

Since we want the partial pressure of MTBE in the gas phase in a closed system (i.e., trapped air), we can write

$$P_{\text{MTBE}} = K_H \times [\text{MTBE}]$$

Methyl-*tert*-butyl ether is $\text{CH}_3\text{-O-C}(\text{CH}_3)_3$ or $\text{C}_5\text{H}_{12}\text{O}$ (MW = 88.0 g/mol).

Solution:

Converting the concentration of MTBE from ppm to mol per m^3 using the MW of 88.0 g/mol and assuming a density of the water of 1000 kg/m^3 yields,

$$[\text{MTBE}] = 175 \frac{\text{mg}}{\text{kg}} \times \frac{1 \text{ mol}}{88.0 \text{ g}} \times \frac{1 \text{ g}}{10^3 \text{ mg}} \times \frac{10^3 \text{ kg}}{\text{m}^3} = 1.99 \frac{\text{mol}}{\text{m}^3}$$

Hence,

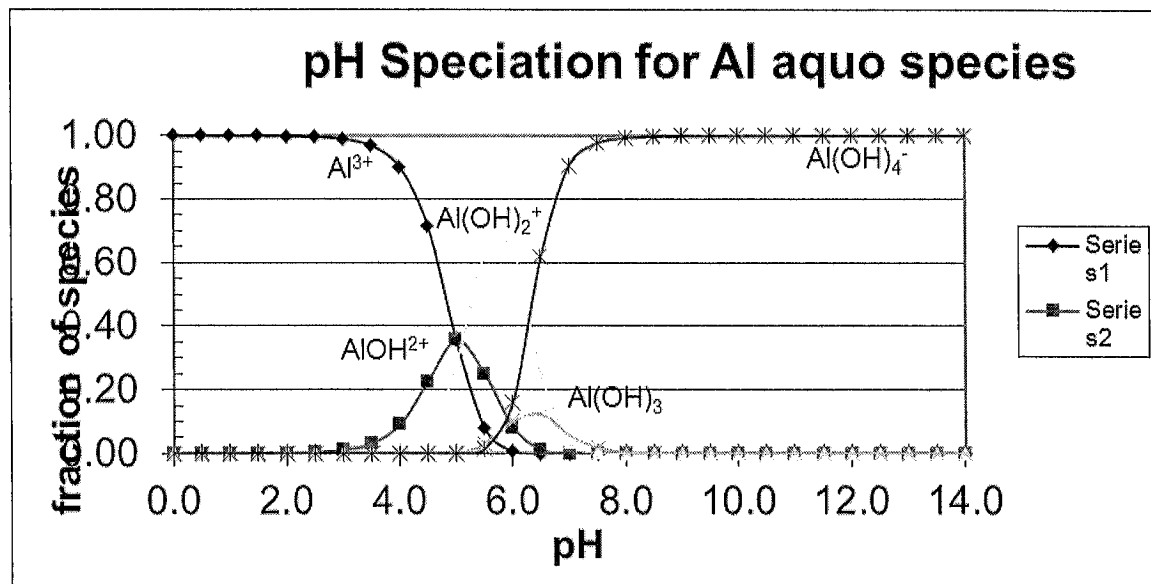
$$P_{\text{MTBE}} = (5.8 \times 10^{-4} \text{ atm m}^3 \text{ mol}^{-1}) (1.99 \text{ mol m}^{-3}) = 1.2 \times 10^{-3} \text{ atm (or 117 Pa)}$$

5. Using the pK_a values below for the aluminum aquo complexes, plot a pH speciation diagram for the $Al^{3+} - Al(OH)^{2+} - Al(OH)_2^+ - Al(OH)_3 - Al(OH)_4^-$ system over the pH range of 0 to 14, using Excel for repetitive calculations. Calculate the fractional abundance of aluminum species at pH 5?

$$pK_{a1} = 5.00 \quad pK_{a2} = 5.10 \quad pK_{a3} = 6.80 \quad pK_{a4} = 5.80$$

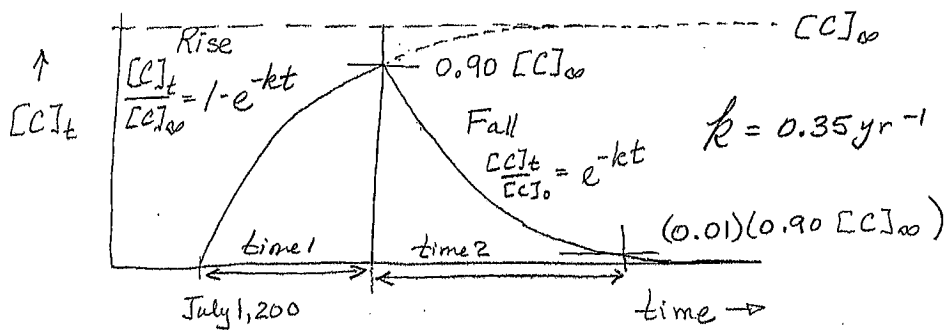
Strategy: Derive expressions for the fractional abundance of each aqueous aluminum species using the appropriate equilibrium expressions to make substitutions as necessary.

Solution: Use Excel to carry out repetitive calculations and plot overlay as below.



6. A pollutant is dumped into a clean lake at a constant rate starting on July 1, 2000. When the pollutant's concentration reaches 90% of its steady state value, the flow of pollutant is stopped. On what date will the concentration of pollutant fall to 1% of its maximum concentration? Assume the rate constants of the increase and decrease are both 0.35 year^{-1} .

Strategy: We need to consider the time for the contaminant to rise to 90% and then fall to 1% of the max conc.



Solution:

$$\text{Rise} \quad \frac{[C]_t}{[C]_{\infty}} = 1 - e^{-kt_1}$$

$$(0.90) = 1 - e^{-(0.35 \text{ yr}) t_1}$$

$$-\ln(0.90 - 1) = -0.35 \text{ yr}^{-1}(t_1)$$

$$\therefore t_1 = \frac{-\ln(0.10)}{-0.35 \text{ yr}^{-1}} = \frac{-2.30}{-0.35 \text{ yr}^{-1}} = 6.58 \text{ yr}$$

Fall

$$\frac{[C]_t}{[C]_0} = e^{-kt_2}$$

$$\frac{(0.01)(0.90 \cancel{[C]_{\infty}})}{(0.90 \cancel{[C]_{\infty}})} = e^{-kt_2}$$

$$\ln(0.01) = -kt_2$$

$$-4.605 = -0.35 \text{ yr}^{-1} (t_2)$$

$$t_2 = \frac{-4.605}{-0.35 \text{ yr}^{-1}} = 13.16 \text{ yr}$$

$$\therefore \text{Total time} = 6.58 + 13.16 \text{ yr} = 19.73 \text{ yrs}$$

July 1, 2019 + 266 days



Mar 23, 2020

7. Consider dissolved organic matter to have a generic formula $\{CH_2O\}$. For a water body containing 1.0 mg/L of DOC, calculate the mass in mg of dissolved oxygen in the same volume of water required to oxidize it completely. Use this calculation to establish a numerical relationship between COD and DOC. Will your result change markedly using the generic formula for dissolved humic material (Fig 12.3, textbook)?



$$\text{mass } O_2 \text{ consumed} = \# \text{ mols } O_2 \text{ consumed} \times \frac{32,000 \text{ mg}}{\text{mol}}$$

$$\# \text{ mols } O_2 \text{ consumed} = \# \text{ mols } CH_2O \text{ consumed}$$

if $DOC = 1.0 \frac{\text{mg C}}{\text{L}}$, then we have

$$1.0 \frac{\text{mg C}}{\text{L}} \times \frac{1 \text{ mol}}{12,000 \text{ mg}} = 8.3 \times 10^{-5} \frac{\text{mols C}}{\text{L}}$$

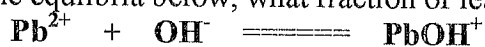
$$\text{and } 8.3 \times 10^{-5} \frac{\text{mols } CH_2O}{\text{L}}$$

so mass of O_2 consumed by $1.0 \frac{\text{mg DOC}}{\text{L}}$

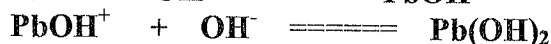
$$\text{is } 8.3 \times 10^{-5} \frac{\text{mol}}{\text{L}} \times \frac{32,000 \text{ mg}}{\text{mol}} = 2.7 \frac{\text{mg}}{\text{L}}$$

$$\text{Therefore, } 1.0 \frac{\text{mg DOC}}{\text{L}} = \frac{2.7 \text{ mg } O_2}{\text{L}} \quad \text{i.e. } \boxed{COD = 2.7 \text{ DOC}}$$

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



$$K = 2.0 \times 10^6$$



$$K = 4.0 \times 10^4$$

$\leftarrow K_{f1}$
 $\leftarrow K_{f2}$

strategy: The reactions given are written as formation reactions showing the complexation of Pb^{2+} ions with OH^- ligands.

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

\uparrow substitute of simplify expression
 \uparrow

\leftarrow sum of all Pb containing species under consideration

Solution:

$$\text{Since } K_1 = \frac{[\text{PbOH}^+]}{[\text{Pb}^{2+}][\text{OH}^-]} = 2.0 \times 10^6$$

$$\text{we can write } [\text{PbOH}^+] = K_{f1}[\text{Pb}^{2+}][\text{OH}^-]$$

$$\text{and } [\text{Pb(OH)}_2] = K_{f2}[\text{PbOH}^+][\text{OH}^-]$$

$$\text{So } \alpha_{\text{Pb}^{2+}} = \frac{[\text{Pb}^{2+}]}{[\text{Pb}^{2+}] + K_{f1}[\text{Pb}^{2+}][\text{OH}^-] + K_{f2}[\text{PbOH}^+][\text{OH}^-]}$$

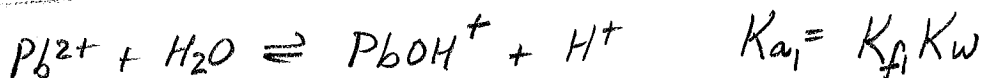
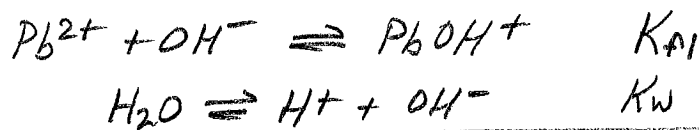
$$= \frac{1}{1 + K_{f1}[\text{OH}^-] + K_{f2}[\text{OH}^-]}$$

$$\text{at pH} = 7, [\text{OH}^-] = 1.0 \times 10^{-7}$$

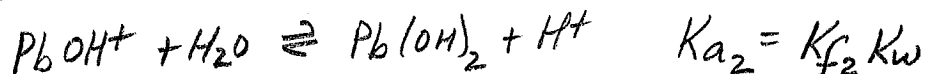
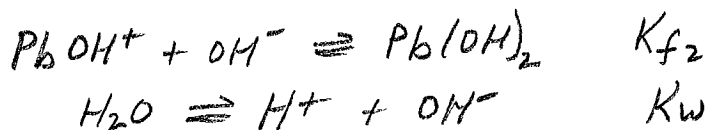
$$\text{So } \alpha_{\text{Pb}^{2+}} = \frac{1}{1 + (2.0 \times 10^6)(1.0 \times 10^{-7}) + (4.0 \times 10^4)(1.0 \times 10^{-7})}$$

$$= \frac{1}{1 + 0.2 + 0.004} = \frac{1}{1.204} = 0.83 \text{ (83\%)}$$

Alternatively, one could convert the given formation reactions to the more familiar acid dissociation reactions.

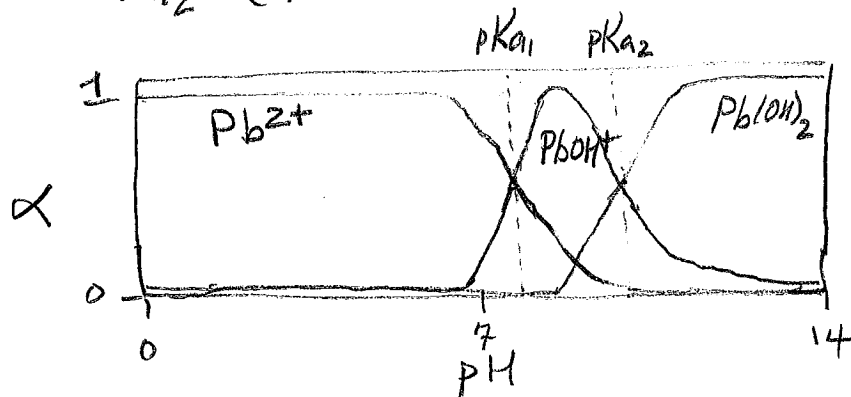


and



where $K_{a1} = (2.0 \times 10^6)(1.0 \times 10^{-14}) = 2.0 \times 10^{-8}$ s/ $\text{p}K_{a1} = 7.7$

and $K_{a2} = (4.0 \times 10^4)(1.0 \times 10^{-14}) = 2.0 \times 10^{-10}$ s/ $\text{p}K_{a2} = 9.7$



$$\alpha_{\text{Pb}^{2+}} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}} \quad (\text{derived in class for diprotic acids})$$

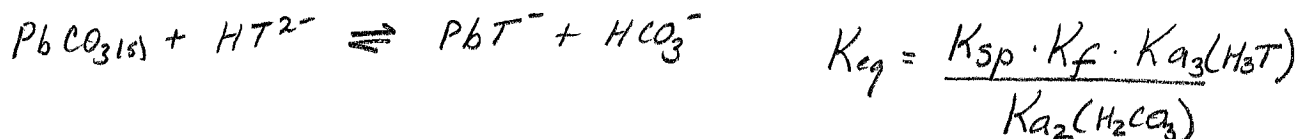
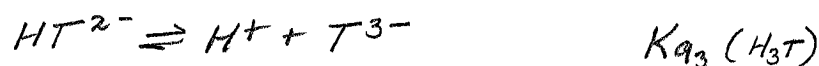
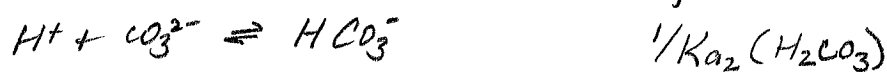
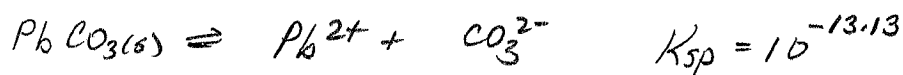
$$\begin{aligned} &= \frac{1.0 \times 10^{-14}}{(1.0 \times 10^{-14}) + (2.0 \times 10^{-8})(1.0 \times 10^{-7}) + (2.0 \times 10^{-8})(2.0 \times 10^{-10})} \\ &= 0.83 \end{aligned}$$

9. 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 $[\text{HCO}_3^-] = 1.25 \times 10^{-3} \text{ M}$.



strategy: Combine simpler equilibria processes to derive an equilibrium constant for the above reaction and solve for $\frac{[\text{HT}^{2-}]}{[\text{HT}^{2-}] + [\text{PbT}^-]}$

Solution:



$$K_{\text{eq}} = \frac{[\text{PbT}^-][\text{HCO}_3^-]}{[\text{HT}^{2-}]} = 0.0181$$

$$= 0.0181$$

where $K_{\text{a}_3}(\text{H}_3\text{T}) = 10^{-10.28}$

and $K_{\text{a}_2}(\text{H}_2\text{CO}_3) = 4.7 \times 10^{-11}$

$$\therefore [\text{HT}^{2-}] = \frac{[\text{PbT}^-][\text{HCO}_3^-]}{0.0181}$$

$$= [\text{PbT}^-] \left(\frac{1.25 \times 10^{-3}}{0.0181} \right)$$

$$= (6.91 \times 10^{-2}) [\text{PbT}^-]$$

$$\text{So } \frac{[\text{HT}^{2-}]}{[\text{HT}^{2-}] + [\text{PbT}^-]} = \frac{0.0691 [\text{PbT}^-]}{0.0691 [\text{PbT}^-] + [\text{PbT}^-]} = \frac{0.0691}{1.0691}$$

$$= 0.065 \text{ (6.5\%)}$$

class notes

10. A woodwaste leachate sample has a Fe(II) concentration of 20 mg/L and a dissolved organic matter concentration of 50 mg/L. Using a typical value for the concentration of carboxylate ions of per gram of DOM given in the textbook and the conditional formation constant between Fe^{2+} and fulvic acid of 5×10^3 at pH 5, calculate the fraction of iron (II) complexed to the dissolved organic matter at pH 5. How would you expect your answer to change if the actual pH of the leachate were 7 rather than 5? Explain.

strategy: Use equilibrium between fulvic acid carboxylates (FAco_2^-) and iron (II), to determine

fraction as
$$\frac{[\text{FAco}_2^- \text{Fe}]}{[\text{Fe(II)}]_T} = \frac{[\text{FAco}_2^- \text{Fe}]}{[\text{Fe}^{2+}] + [\text{FAco}_2^- \text{Fe}]}$$

Solution:



$$K_f = \frac{[\text{FAco}_2^- \text{Fe}]}{[\text{Fe}^{2+}][\text{FAco}_2^-]} \quad \left. \vphantom{K_f} \right\} \text{remember, these are equilibrium concentrations}$$

$$[\text{Fe(II)}]_T = [\text{Fe}^{2+}] + [\text{FAco}_2^- \text{Fe}] = 20 \text{ mg/L} \times \frac{1 \text{ mol}}{55.85 \text{ g}} \times \frac{1 \text{ g}}{10^3 \text{ mg}} = 3.58 \times 10^{-4} \text{ mol/L}$$

$[\text{DOM}] = 50 \text{ mg/L}$, but we need $[\text{FAco}_2^-]$ (use $[\text{FAco}_2^-] = 4.4 \frac{\text{mmol}}{\text{g DOM}}$)
Pg. 284 (text)

$$[\text{FAco}_2^-]_T = \frac{4.4 \times 10^{-3} \text{ mol FAco}_2^-}{1 \text{ g DOM}} \times \frac{50 \times 10^{-3} \text{ g DOM}}{\text{L}} = \frac{2.2 \times 10^{-4} \text{ mol FAco}_2^-}{\text{L}}$$

$$\text{So } [\text{Fe}^{2+}]_{\text{eq}} = [\text{Fe}^{2+}]_T - [\text{FAco}_2^- \text{Fe}]_{\text{eq}}$$

$$\text{and } [\text{FAco}_2^-]_{\text{eq}} = [\text{FAco}_2^-]_T - [\text{FAco}_2^- \text{Fe}]_{\text{eq}}$$

if we let 'x' represent the concentration of fulvic acid complexed to iron (II) in solution, we can write

$$[\text{Fe}^{2+}]_{\text{eq}} = \left(3.58 \times 10^{-4} \frac{\text{mol}}{\text{L}} - x\right)$$

$$[\text{FAco}_2^-]_{\text{eq}} = \left(2.2 \times 10^{-4} \frac{\text{mol}}{\text{L}} - x\right)$$

$$\text{and } \therefore K_f = \frac{x}{(3.58 \times 10^{-4} - x)(2.2 \times 10^{-4} - x)} = 5 \times 10^3$$

$$\frac{x}{7.88 \times 10^{-8} - 3.58 \times 10^{-4} x - 2.2 \times 10^{-4} x + x^2} = 5 \times 10^3$$

$$\frac{x}{7.88 \times 10^{-8} - 5.78 \times 10^{-4} x + x^2} = 5 \times 10^3$$

$$x = 3.94 \times 10^{-4} - 2.89x + 5 \times 10^3 x^2$$

$$\therefore 5000 x^2 - 3.89x + 3.94 \times 10^{-4} = 0$$

use quadratic formula to solve for 'x'

where $a = 5000$; $b = -3.89$; $c = 3.94 \times 10^{-4}$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$\therefore x = 6.5 \times 10^{-4} \text{ M}$$

invalid since $> [\text{FAco}_2^-]_{\text{T}}$

$$\text{or } x = \underline{1.2 \times 10^{-4} \text{ M}}$$

$$= [\text{FAco}_2^- \text{Fe}]$$

Therefore, the fraction of iron(II) complexed to FA is

given by,
$$\frac{1.2 \times 10^{-4} \text{ M}}{3.58 \times 10^{-4} \text{ M}} = 0.335 \text{ (34\%)}$$

At higher pH, there are several things to consider. First, the speciation of aqueous Fe(II) species, and second, the speciation of the fulvic acid carboxylate ions.

Fe(II) is not very acidic (ie. K_{a1} & $K_{a2} \ll 10^{-7}$) therefore, $\text{Fe}^{2+}(\text{aq})$ dominates at both pH 5 and pH 7.

However, FAco_2^- is in equilibrium with the protonated form (ie. FAco_2H). The pKa for carboxylic acids is around 5. Therefore, FAco_2^- are partially protonated at pH 5 (the pH at which the formation constant was reported), but largely deprotonated at pH 7. Hence, we expect a greater degree of complexation as pH increases.