

# CHEM 301

## Assignment #3

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

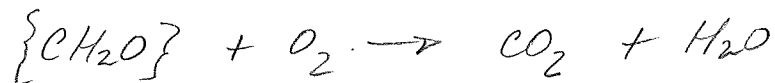
Clearly state assumptions and reference sources for any constants used.

Due date: November 22<sup>nd</sup>.

Attempt all questions. Only even numbers will be graded.

1. Calculate the mass of carbohydrate with the generic formula  $\{CH_2O\}$  required to consume the dissolved oxygen from 1.0 L of water initially in equilibrium with the atmosphere at 12 °C, to hypoxic conditions ( $< 2.0$  mg/L). Will your result change markedly using the formula for dissolved humic material (Fig 12.3, textbook)? Will a water sample with this mass of carbohydrate necessarily become hypoxic? What other factors influence the oxygen status of the water?

Strategy: determine conc. of  $O_2(aq)$  in satd. solution at 12°C and calculate the #mols of  $O_2(aq)$  consumed to reach 2.0 mg/L. Then use balanced chemical equation



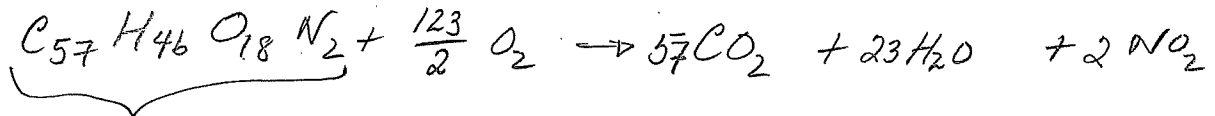
Solution: Using Fig. 11.1 (textbook), we see that at 12°C, the equilibrium conc. of  $O_2(aq)$  in freshwater is 11.0 mg/L. Therefore, to reach hypoxic conditions, we have  $11.0 - 2.0 = 9.0 \frac{mg}{L} O_2$  consumed. In 1.0L liters of solution, this corresponds to;

$$9.0 \frac{mg}{L} \times \frac{1 \text{ mol}}{32,000 \text{ mg}} = 2.8 \times 10^{-4} \text{ mols } O_2$$

Therefore,  $2.8 \times 10^{-4}$  mols of  $\{CH_2O\}$  will consume this  $O_2(aq)$ .

$$\begin{aligned} \text{Mass } \{CH_2O\} &= 2.8 \times 10^{-4} \text{ mols } O_2 \times \frac{1 \text{ mol } \{CH_2O\}}{1 \text{ mol } O_2} \times 30,000 \frac{mg}{mol} \\ &= 8.4 \text{ mg} \end{aligned}$$

Using generic formula in Fig 12-3 (textbook),  $n=1$



$$\text{MW} = 1046 \text{ g/mol}$$

$$\# \text{mols } C_{57}H_{46}O_{18}N_2 = \# \text{mols } O_2 \times \frac{1 \text{ mol } C_{57}H_{46}O_{18}N_2}{(123/2) \text{ mols } O_2}$$

$$= 2.8 \times 10^{-4} \text{ mols } O_2 \times \frac{1 \text{ mol } C_{57}H_{46}O_{18}N_2}{61.5 \text{ mols } O_2}$$

$$= 4.6 \times 10^{-6} \text{ mols } C_{57}H_{46}O_{18}N_2$$

$$\therefore \text{mass } C_{57}H_{46}O_{18}N_2 = 4.6 \times 10^{-6} \text{ mols} \times \frac{1046 \text{ g}}{\text{mol}}$$

$$= 4.8 \text{ mg}$$

2. A water sample is known to have a pH of 8.44, calcium hardness of 165 ppm  $\text{CaCO}_3$  and a total alkalinity of 168 ppm as  $\text{CaCO}_3$ .

a) Calculate the total inorganic carbon and report concentration of the carbonate ion  $[\text{CO}_3^{2-}]$ .

b) Calculate the pH at which this sample is saturated with respect to calcite and determine the saturation state with respect to calcite for this sample.

$$K_{sp}(\text{calcite}) = 3.36 \times 10^{-9}$$

a) Total inorganic carbon

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

Use  $[\text{alk}]_T$  to determine either  $[\text{HCO}_3^-]$  or  $[\text{CO}_3^{2-}]$

$$[\text{alk}]_T = \frac{168 \text{ mg CaCO}_3}{\text{L}} \times \frac{1 \text{ mol}}{100,000 \text{ mg}} \times \frac{2 \text{ mol H}^+}{1 \text{ mol CaCO}_3} = 3.36 \times 10^{-3} \frac{\text{mol}}{\text{L}}$$

$$[\text{H}^+] = 10^{-8.44} = 3.63 \times 10^{-9} \frac{\text{mol}}{\text{L}}$$

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

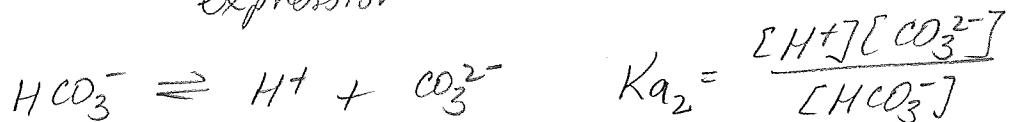
$$\uparrow$$

$$3.36 \times 10^{-3}$$

two variables  
∴ use  $K_{a2}$   
expression

$$\uparrow$$

from pH ( $[\text{OH}^-] = 10^{-5.56}$ )



$$\therefore [\text{HCO}_3^-] = \frac{3.63 \times 10^{-9} [\text{CO}_3^{2-}]}{4.7 \times 10^{-11}}$$

Substituting into  $[\text{alk}]_T$

$$= 77.2 [\text{CO}_3^{2-}]$$

$$3.36 \times 10^{-3} = 77.2 [\text{CO}_3^{2-}] + 2 [\text{CO}_3^{2-}] + 10^{-5.56}$$

$$79.2 [\text{CO}_3^{2-}] = 3.36 \times 10^{-3} - 2.75 \times 10^{-6}$$

$$\therefore [\text{CO}_3^{2-}] = 4.24 \times 10^{-5} \text{ M}$$

So total inorganic carbon

$$\begin{aligned}
 [\text{CO}_2(\text{aq})]_T &= [\text{CO}_2(\text{aq})] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \\
 &\quad \uparrow \qquad \qquad \quad \uparrow \qquad \qquad \quad \uparrow \\
 &\quad \text{from } K_{a1} \quad 77.2[\text{CO}_3^{2-}] \quad 4.24 \times 10^{-5} \text{ M} \\
 &\quad \text{expression} \quad = 3.27 \times 10^{-3} \text{ M} \quad (\text{above}) \\
 &\qquad \qquad \qquad \quad (\text{above})
 \end{aligned}$$

$$\begin{aligned}
 K_{a1} &= \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2(\text{aq})]} \\
 \therefore [\text{CO}_2(\text{aq})] &= \frac{[\text{H}^+][\text{HCO}_3^-]}{K_{a1}} \\
 &= \frac{(3.63 \times 10^{-9})(3.27 \times 10^{-3})}{4.5 \times 10^{-7}} \\
 &= 2.64 \times 10^{-5}
 \end{aligned}$$

$$\begin{aligned}
 \therefore [\text{CO}_2(\text{aq})]_T &= (2.64 \times 10^{-5} + 3.27 \times 10^{-3} + 4.24 \times 10^{-5}) \text{ M} \\
 &= 3.34 \times 10^{-3} \text{ M}
 \end{aligned}$$

Note: If you used  $K_H P_{\text{CO}_2}$  to calculate  $[\text{CO}_2(\text{aq})]$ , you would underestimate its concentration by a factor  $\sim 2 \times$ . Remember, in natural system in contact with  $\text{CaCO}_3(\text{s})$  and decomposition of organic matter, there are additional sources of  $\text{CO}_2(\text{aq})$ .

$$b) \quad \Omega_{CaCO_3} = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}}$$

Saturated when  $[Ca^{2+}][CO_3^{2-}] = K_{sp}$

$$[CO_3^{2-}] = \frac{3.36 \times 10^{-9}}{[Ca^{2+}]}$$

↑

from 165 ppm  $CaCO_3$  hardness

$$\begin{aligned} [Ca^{2+}] &= 165 \frac{mg \text{ } CaCO_3}{L} \times \frac{1 \text{ mol}}{100,000 \text{ mg}} \times \frac{1 \text{ mol } Ca^{2+}}{1 \text{ mol } CaCO_3} \\ &= 1.65 \times 10^{-3} \frac{\text{mol}}{L} \end{aligned}$$

$$\therefore [CO_3^{2-}] \text{ at saturation} = \frac{3.36 \times 10^{-9}}{1.65 \times 10^{-3}} = 2.04 \times 10^{-6} \text{ M}$$

We need pH at which

$$\alpha_{CO_3^{2-}} = \frac{2.04 \times 10^{-6}}{[CO_2(aq)]_T} = 6.1 \times 10^{-4}$$

↑  
 $3.34 \times 10^{-3} \text{ M}$  (above)

$$\alpha_{CO_3^{2-}} = \frac{K_{a1} K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1} K_{a2}}$$

$$6.1 \times 10^{-4} = \frac{2.1 \times 10^{-17}}{x^2 + 4.5 \times 10^{-7} x + 2.1 \times 10^{-17}}$$

where  $x$   
 represents  
 $[H^+]$

$$6.1 \times 10^{-4} x^2 + 2.7 \times 10^{-10} x + 1.3 \times 10^{-20} = 2.1 \times 10^{-17}$$

$$\underbrace{6.1 \times 10^{-4}}_a x^2 + \underbrace{2.7 \times 10^{-10}}_b x - \underbrace{2.1 \times 10^{-17}}_c = 0$$

Use quadratic formula

$$x = 6.7 \times 10^{-8}$$

$$\therefore [H^+] = 6.7 \times 10^{-8}$$

$$pH = 7.2$$

Note solution is currently oversaturated with respect to  $CaCO_3(s)$  and will remain so until the pH drops to below 7.1

3. Derive an expression for  $[H^+]$  for a water sample in equilibrium with atmospheric carbon dioxide and lithospheric calcium carbonate in terms of the appropriate equilibrium constants and the partial pressure of  $CO_2$ . Show your work and annotate your derivation indicating what you are doing.

*See textbook section 11.2*

*equations 11.10 - 11.19*

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



As gas bubbles evolve at the sediment interface at a depth of 50 meters and remain in contact with water at the sediment surface long enough so that equilibrium is attained, calculate the aqueous molar concentration of methane in the interstitial sediment pore water. Assume a total pressure at this depth of 0.61 MPa and a temperature of 5°C.

*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 CH<sub>4</sub> and CO<sub>2</sub>. We can then use the partial pressure of CH<sub>4</sub> inside the gas bubble and the corresponding Henry's law constant to calculate the concentration of aqueous CH<sub>4</sub> at equilibrium in the pore water.

*Solution:*

The aqueous concentration of methane is given by the Henry's Law expression;

$$[\text{CH}_4(\text{aq})] = K_H \times P_{\text{CH}_4(\text{g})}$$

Where  $K_H$  is for methane at 5°C (278 K) and  $P_{\text{CH}_4}$  is given by;

$$P_T = 0.61 \text{ MPa} = P_{\text{CO}_2} + P_{\text{CH}_4}$$

and  $P_{\text{CO}_2} = P_{\text{CH}_4} = 0.305 \text{ MPa}$

(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).

In order to 'solve' this problem, we need to calculate  $K_H$  for CH<sub>4</sub> at 278K. Since the  $K_H$  value for methane (textbook, Table 11.1) is reported at 25°C (298K), we will need to adjust to a lower temperature (recall; gases are more water soluble at lower temperature, so we expect  $K_H$  to be greater at 278K than at 298K).

Recall, all equilibrium constants are temperature dependent and this dependence can be expressed as a variation of the Clausius – Clapeyron equation.

$$\ln \left( \frac{K_{T_2}}{K_{T_1}} \right) = \frac{-\Delta H_{\text{rxn}}^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

where  $T_1 = 298\text{K}$ ,  $T_2 = 278\text{K}$ ,  $K_{T_1} = 1.4 \times 10^{-8} \text{ M Pa}^{-1}$ ,  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $\Delta H_{\text{rxn}}^\circ =$  enthalpy change for the aqueous dissolution of methane at std state conditions and  $K_{T_2} =$  Henry's law constant for methane at 278K.



$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= [\Delta H_f^\circ(\text{CH}_4(\text{aq}))] - [\Delta H_f^\circ(\text{CH}_4(\text{g}))] = (-89.04 \text{ kJ mol}^{-1}) - (-74.80 \text{ kJ mol}^{-1}) \\ &= -14.24 \text{ kJ mol}^{-1} \text{ (Water Chemistry, M. Benjamin, Appendix A1, p635)} \end{aligned}$$



Therefore,

$$\ln\left(\frac{K_{T2}}{K_{T1}}\right) = 0.4135$$

and

$$K_{T2} = K_{T1} e^{(0.4135)} = 2.12 \times 10^{-8} \text{ M Pa}^{-1}$$

From the Henry's Law expression;

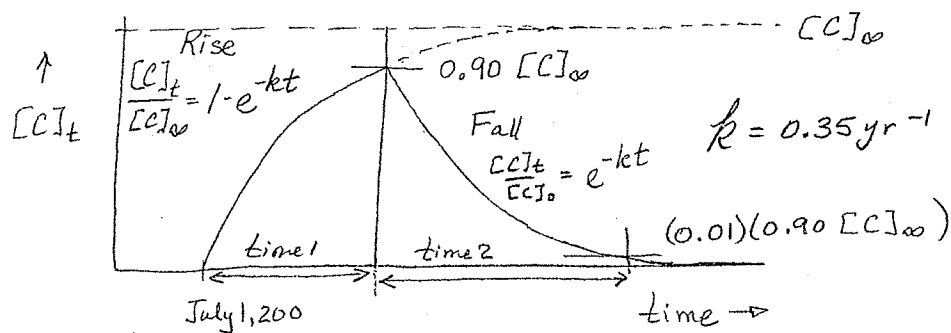
$$[\text{CH}_4(\text{aq})] = K_H \times P_{\text{CH}_4}$$

Using the  $K_H$  calculated above yields;

$$[\text{CH}_4(\text{aq})] = 2.12 \times 10^{-8} \text{ M Pa}^{-1} \times 305,000 \text{ Pa} = 6.5 \text{ mM}$$

5. A pollutant is dumped into a clean lake at a constant rate starting on July 1, 2018. 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  $0.35 \text{ year}^{-1}$ .

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



Solution:

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

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

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

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

Fall

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

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

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

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

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

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

July 1, 2019 + 266 days



Mar 23, 2020

6. A natural water from a northern Ontario bog with a pH = 6.15 has a TOC determined to be 7.5 mg/L of C. The charge imbalance [ $\Sigma(-ve) - \Sigma(+ve)$ ] = 52  $\mu\text{mol/L}$ . Estimate the concentration of DOM (mg/L) and the number of carboxyl groups per gram of DOM ( $\mu\text{mol/g}$ ).

TOC is measured as mass of Carbon whereas DOM is mass of material. Since DOM is roughly 60% Carbon by mass, we can say

$$7.5 \frac{\text{mg C}}{\text{L}} \times \frac{1 \text{ g DOM}}{0.6 \text{ g C}} = 12.5 \frac{\text{mg DOM}}{\text{L}}$$

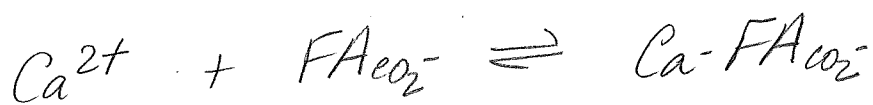
assuming the charge imbalance is due to carboxyl groups ( $\text{FAco}_2^-$ ), we can write

$$52 \times 10^{-6} \frac{\text{mol FAco}_2^-}{\text{L}} \times \frac{1 \text{ L}}{12.5 \text{ mg DOM}} \times \frac{10^3 \text{ mmol}}{\text{mol}} \times \frac{10^3 \text{ mg}}{\text{g}}$$

$$= 4.2 \frac{\text{mmol FAco}_2^-}{\text{g DOM}}$$

7. Calculate the percent of fulvic acid bound to calcium in a lake sample containing 36 mg/L of calcium and 12  $\mu\text{g/L}$  of DOM (as fulvic acid). Use the conditional stability constants in Table 13.3 and assume  $\text{Ca}^{2+}$  is the only metal present in significant concentration and a pH of 5.

strategy: convert concentrations to  
 mols/L for both  $\text{Ca}^{2+}$  and  $\text{FAco}_2^-$   
 Use equilibrium expression  
 for complexation



$$K'_f = \frac{[\text{Ca-FAco}_2^-]}{[\text{Ca}^{2+}]_f [\text{FAco}_2^-]_f} = 1.2 \times 10^3$$

$$[\text{Ca}^{2+}]_T = 36 \text{ mg/L} \times \frac{1 \text{ mol}}{40,078 \text{ mg}} = 9.0 \times 10^{-4} \text{ M}$$

$$= [\text{Ca}^{2+}]_f + [\text{Ca-FAco}_2^-]$$

$$[\text{FAco}_2^-]_T = 12 \text{ } \mu\text{g/L} \times \frac{5.0 \times 10^{-3} \text{ mol CO}_2^-}{9} \times \frac{1 \text{ g}}{10^6 \text{ } \mu\text{g}}$$

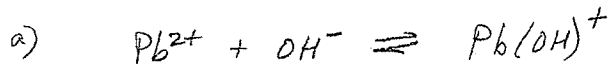
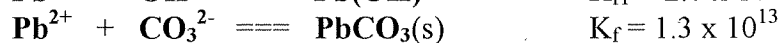
$$= 6.0 \times 10^{-8} \text{ M}$$

$$= [\text{FAco}_2^-]_f + [\text{Ca-FAco}_2^-]$$

8. The stepwise formation constants for  $\text{Pb(OH)}^+$  and  $\text{PbCO}_3$  are given below. For a solution containing  $10^{-6} \text{ M Pb}_T$ , calculate the pH of the speciation boundary between  $\text{Pb}^{2+}$  and

a)  $\text{PbOH}^+$  in pure water

b)  $\text{PbCO}_3$  for a solution containing  $10^{-3} \text{ M CO}_3^{2-}$



$$K_{f1} = \frac{[\text{Pb(OH)}^+]}{[\text{Pb}^{2+}][\text{OH}^-]}$$

at boundary,  $[\text{Pb(OH)}^+] = [\text{Pb}^{2+}]$

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

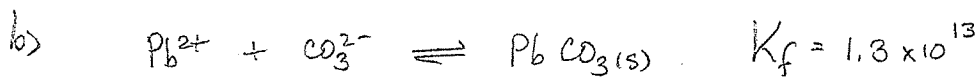
$$\text{and } [\text{OH}^-] = \frac{1}{2.0 \times 10^6} = 5.0 \times 10^{-7} \text{ M}$$

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

$$\text{So } [\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{5.0 \times 10^{-7}}$$

$$= 2.0 \times 10^{-8} \text{ M}$$

$$\text{pH} = 7.7$$



$$K_f = \frac{1}{[\text{Pb}^{2+}][\text{CO}_3^{2-}]} = 1.3 \times 10^{13}$$

If we assume that  $[\text{Pb}^{2+}] \approx [\text{Pb}^{2+}]_T$  at these conditions, we can calculate

$$\begin{aligned} [\text{CO}_3^{2-}] &= \frac{1}{[\text{Pb}^{2+}](1.3 \times 10^{13})} = \frac{1}{(10^{-6})(1.3 \times 10^{13})} \\ &= 7.7 \times 10^{-8} \text{ M} \quad \left\{ \begin{array}{l} \text{this will be true, if} \\ \text{pH} < \text{p}K_{a1} \text{ for } \text{Pb}^{2+} \text{ (ie } 7.7) \end{array} \right\} \end{aligned}$$

Since  $[\text{CO}_3^{2-}]_T = 1.0 \times 10^{-3} \text{ M}$ , we see that only a small fraction of inorganic carbon is present as  $\text{CO}_3^{2-}$ . In fact, we can write

$$\alpha_{\text{CO}_3^{2-}} = \frac{K_{a1} K_{a2}}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1} K_{a2}} = \frac{7.7 \times 10^{-8}}{10^{-3}} = 7.7 \times 10^{-5}$$

Solving for  $[\text{H}^+]$  using quadratic formula yields;

$$\frac{(4.5 \times 10^{-7})(4.7 \times 10^{-11})}{[\text{H}^+]^2 + (4.5 \times 10^{-7})[\text{H}^+] + (4.5 \times 10^{-7})(4.7 \times 10^{-11})} = 7.7 \times 10^{-5}$$

$$\frac{2.12 \times 10^{-17}}{[H^+]^2 + (4.5 \times 10^{-7}) [H^+] + 2.12 \times 10^{-17}} = 7.7 \times 10^{-5}$$

let 'x' represent  $[H^+]$

$$7.7 \times 10^{-5} x^2 + 3.47 \times 10^{-11} x + 1.63 \times 10^{-21} = 2.12 \times 10^{-17}$$

$$7.7 \times 10^{-5} x^2 + 3.47 \times 10^{-11} x - 2.12 \times 10^{-17} = 0$$

$$\begin{array}{ccc} \uparrow & \uparrow & \uparrow \\ a & b & c \end{array}$$

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

$$= \frac{-3.47 \times 10^{-11} \pm \left[ (3.47 \times 10^{-11})^2 - 4(7.7 \times 10^{-5})(-2.12 \times 10^{-17}) \right]^{1/2}}{2(7.7 \times 10^{-5})}$$

$$= \frac{-3.47 \times 10^{-11} \pm (8.79 \times 10^{-11})}{1.54 \times 10^{-4}}$$

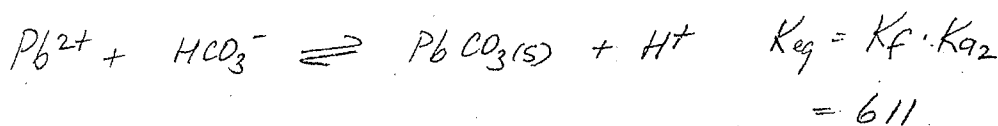
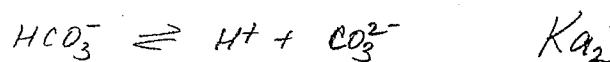
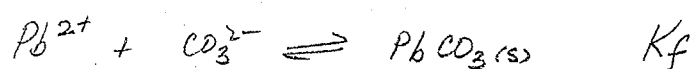
$$= 3.45 \times 10^{-7} M \Rightarrow [H^+]$$

$$\therefore \boxed{pH = 6.4}$$

Since pH is less than  $pK_{a1}$  for  $Pb^{2+}$ , these assumption regarding  $[Pb^{2+}] \approx [Pb]_T$  is valid.



An alternate approach to Q (b) is to combine the formation constant reaction with a protonation/deprotonation step so that  $[H^+]$  or  $[OH^-]$  appears in the equilibrium expression.



$$K_{eq} = \frac{[H^+]}{[Pb^{2+}][HCO_3^-]}$$

if we assume that  $[Pb^{2+}] \approx [Pb]_T = 10^{-6} M$   
and further, that  $[HCO_3^-] \approx [CO_3^{2-}]_T = 10^{-3} M$

then we get

$$[H^+] = K_{eq} \cdot [Pb^{2+}][HCO_3^-] = 6.11 \times 10^{-7} M$$

$$\text{and } pH = 6.2$$

Our assumption for  $[Pb^{2+}]$  is okay since  $pH < pK_{a1}(Pb^{2+})$   
but, we are quite near  $pK_{a1}$  for  $H_2CO_3$ , so this calculated value should be taken as an estimate

9. Using the CO2Sys\_v2.3 software, calculate the pH, the  $P_{\text{CO}_2}$ , inorganic carbon concentrations, and the aragonite saturation ( $\Omega_{\text{Ar}}$ ) at output conditions of 4 °C, total pressure of 1000 dbars of pressure (~1000 m depth), for a water sample with a measured total alkalinity of 1400  $\mu\text{mol}/\text{kg}(\text{sw})$ , and total carbonate of 1275  $\mu\text{mol}/\text{kg}(\text{sw})$  at input conditions of 20 °C, 0 dbar pressure (surface), 0.3  $\mu\text{mol}/\text{kg}(\text{sw})$  total P and 1  $\mu\text{mol}/\text{kg}(\text{sw})$  Si, and a salinity of 30. Use this program to estimate the saturation horizon depth under these conditions. Specify the choice of constants used and any other assumptions.

[http://cdiac.ess-dive.lbl.gov/ftp/oceans/co2sys/CO2SYS\\_calc\\_XLS\\_v2.3/](http://cdiac.ess-dive.lbl.gov/ftp/oceans/co2sys/CO2SYS_calc_XLS_v2.3/)

*see on-line spreadsheet*

10. Determine the fraction of  $\text{Zn}^{2+}$  and  $\text{T}^{3-}$  (from nitrilotriacetate) in water at pH 8.50 from the corresponding acid dissociation constants. Estimate the ratio of Zn-complexed NTA to total NTA in a wastewater sample with a total NTA concentration of  $100. \mu\text{g L}^{-1}$  containing 2.0 ppm of zinc.

$$\log K_f(\text{ZnT}^-) = 10.66$$

Consider the species possible  $\text{Zn}^{2+} / \text{ZnOH}^+ / \text{Zn}(\text{OH})_2 / \text{Zn}(\text{OH})_3^-$

Since  $pK_{a1}$  for  $\text{Zn}^{2+}$  is given as 9.60 (text) Table 13.1

The dominant form is  $\text{Zn}^{2+}$  at pH = 8.50

We can estimate  $\alpha_{\text{Zn}^{2+}} \approx 0.9$  since we are approx. 1 pH unit below the  $pK_{a1}$  for  $\text{Zn}^{2+}$ .

For NTA, the possible forms are  $\text{H}_3\text{T} / \text{H}_2\text{T}^- / \text{HT}^{2-} / \text{T}^{3-}$

Since  $pK_{a1} = 1.66$ ,  $pK_{a2} = 2.95$ ,  $pK_{a3} = 10.28$  (text, p. 305)

We see that the dominant form of NTA at

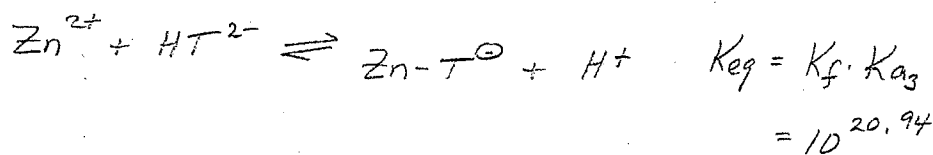
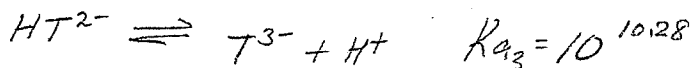
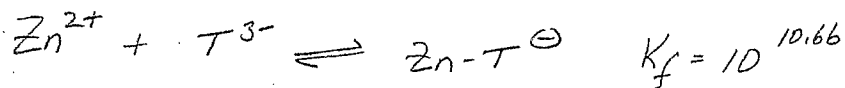
pH = 8.50 is  $\text{HT}^{2-}$ . We can estimate

$\alpha_{\text{HT}^{2-}} \approx 0.99$  since we approx. 2 pH units below  $pK_{a3}$  for NTA.

$$\frac{[\text{Zn-T}^\ominus]}{[\text{NTA}]_T} \leftarrow ?$$

$$[\text{NTA}]_T \leftarrow 100. \mu\text{g/L} \times \frac{1 \text{ mol}}{191 \text{ g}} \times \frac{1 \text{ g}}{10^6 \mu\text{g}} = 5.24 \times 10^{-7} \text{ M}$$

$$\text{and } [\text{Zn}]_T = 2.0 \frac{\text{mg}}{\text{L}} \times \frac{1 \text{ mol}}{65.38 \text{ g}} \times \frac{1 \text{ g}}{10^3 \text{ mg}} = 3.1 \times 10^{-5} \text{ M}$$



$$= 10^{20.94}$$

$$= 8.71 \times 10^{20}$$

$$K_{eq} = \frac{[\text{Zn-T}^\ominus][\text{H}^+]}{[\text{Zn}^{2+}][\text{HT}^{2-}]} = 8.71 \times 10^{20}$$

$$\text{where } [\text{H}^+] = 10^{-8.50} = 3.16 \times 10^{-9} \text{ M}$$

$$[\text{HT}^{2-}] = [\text{NTA}]_T - [\text{Zn-T}^\ominus]$$

$$[\text{Zn}^{2+}] = [\text{Zn}]_T - [\text{Zn-T}^\ominus]$$

Let 'x' represent  $[\text{Zn-T}^\ominus]$ , then we can write

$$\frac{(x)(3.16 \times 10^{-9})}{(3.1 \times 10^{-5} - x)(5.2 \times 10^{-7} - x)} = 8.71 \times 10^{20}$$

Solve for 'x' using quadratic formula or  
make simplifying assumption

Since  $[Zn^{2+}]_T \gg [NTA]_T$

then  $[Zn^{2+}] \approx [Zn]_T = 3.1 \times 10^{-5} M$

and we can write

$$\frac{(x)(3.16 \times 10^{-9})}{(3.1 \times 10^{-5})(5.2 \times 10^{-7} - x)} \approx 8.71 \times 10^{20}$$

$$3.16 \times 10^{-9} x = 1.40 \times 10^{10} - 2.70 \times 10^{16} x$$

$$2.70 \times 10^{16} x = 1.40 \times 10^{10}$$

$$x = 5.2 \times 10^{-7} M \Rightarrow [Zn-T^{\ominus}]$$

Therefore,  $\frac{[Zn-T^{\ominus}]}{[NTA]} \approx 1$

and nearly 100% of the NTA  
is complexed to  $Zn^{2+}$  under  
these conditions.