Provide solutions to the following questions in a neat and well organized manner. 
Clearly state assumptions and reference sources for any constants used.
Only even numbered questions will be graded.
Due date: November 13th.

1. A water sample is known to have a pH of 8.44 and a total alkalinity of 168 ppm as CaCO₃. Calculate the total inorganic carbon and report the molar concentration of the carbonate ion [CO₃²⁻].

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

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

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

\[
3.36 \times 10^{-3} \quad \uparrow 
\]

\[
10^{-5.56}
\]

Use Ka₂ expression to relate HCO₃⁻ & CO₃²⁻

\[
\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \quad \text{Ka}_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}
\]

\[
[\text{HCO}_3^-] = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{\text{Ka}_2} = \frac{3.63 \times 10^{-9}}{4.7 \times 10^{-11}} = 77.2 \text{ [CO}_3^{2-}] \]

So, re-writing [alk]ₜ yields,

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

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

\[
[\text{CO}_3^{2-}] = \frac{3.36 \times 10^{-3} \text{ M}}{79.2} = 4.2 \times 10^{-5} \text{ M}
\]
Total inorganic carbon

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

\[
\text{Use } K_a_1 \text{ expression for } K_{a_1} \text{ of } [\text{CO}_2(aq)]
\]

\[
77.2 \text{ [CO}_3^{2-}] = 3.27 \times 10^{-3} \text{ M}
\]

\[
\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCO}_3^-
\]

\[
K_{a_1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2(\text{aq})]}
\]

\[
\text{and } [\text{CO}_2(\text{aq})] = \frac{[\text{H}^+][\text{HCO}_3^-]}{K_{a_1}}
\]

\[
= \frac{(10^{-8.44})(3.27 \times 10^{-3})}{4.5 \times 10^{-7}}
\]

\[
= 2.64 \times 10^{-5} \text{ M}
\]

\[
[\text{CO}_2(\text{aq})] = (2.64 \times 10^{-5} + 3.27 \times 10^{-3} + 4.24 \times 10^{-5}) \text{ M}
\]

\[
= 3.34 \times 10^{-3} \text{ M}
\]

Note: If you used \( K_{H^+} \cdot P_{CO_2} \) to calculate \([\text{CO}_2(\text{aq})]\), you would underestimate its true by a factor \( \times 2x \). Remember, in a natural water, there are additional sources of \( \text{CO}_2(\text{aq}) \) (i.e. degradation of organic matter and dissolution of carbonate minerals.)
2. You find a value for the $K_H$ of methyl-tert-butyl ether (MTBE) reported as $5.8 \times 10^{-4}$ atm m$^3$ mol$^{-1}$. Convert this to units of M Pa$^{-1}$.

\[ 5.8 \times 10^{-4} \text{ atm m}^3 \text{ mol}^{-1} \times 101,300 \text{ Pa atm}^{-1} = 58,750 \frac{\text{Pa L}}{\text{mol}} \]

inverting this yields $1.70 \times 10^{-5}$ M Pa$^{-1}$
3. Calculate the pH of fog equilibrated with an unlimited supply of air containing 0.25 ppm \( \text{SO}_2 \text{(g)} \). Now extend this calculation by determining the additional \([H^+]\) that will be contributed by the equilibrium concentration of atmospheric \( \text{CO}_2 \text{(g)} \).

**Strategy:** The concentration of aqueous \( \text{SO}_2 \) 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.

\[
\begin{align*}
\text{SO}_2 \text{(g)} & \rightleftharpoons \text{SO}_2 \text{(aq)} & K_H = 1.8 \times 10^{-5} \text{ M Pa}^{-1} \text{ (text, Table 11.1)} \\
\text{SO}_2 \text{(aq)} + \text{H}_2 \text{O} & \rightleftharpoons \text{H}^+ + \text{HSO}_3^- & K_{a1} = 1.72 \times 10^{-2} \text{ (text, App. B1)} \\
\text{HSO}_3^- & \rightleftharpoons \text{H}^+ + \text{SO}_3^{2-} & K_{a2} = 6.43 \times 10^{-8} \text{ (text, App. B1)}
\end{align*}
\]

Assuming a total pressure of one atmosphere, the \( P_{\text{SO}_2} = \chi_{\text{SO}_2} \times P_T = 0.25 \times 10^{-6} \text{ atm} \). Converting the given \( K_H \) into atmospheres yields;

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

Thus, \([\text{SO}_2 \text{(aq)}] = K_H \times P_{\text{SO}_2} = (1.82 \text{ M atm}^{-1}) (0.25 \times 10^{-6} \text{ atm}) = 4.55 \times 10^{-7} \text{ M}\)

Using the \( K_{a1} \) expression and assuming no further dissociation of \( \text{HSO}_3^- \) (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 \( \text{SO}_2 \text{(aq)} \)

\[
\therefore [\text{H}^+]^2 = (1.72 \times 10^{-2}) (4.55 \times 10^{-7})
\]

so

\[
[\text{H}^+] = 8.85 \times 10^{-5} \text{ M}
\]

\[
\therefore \text{pH} = 4.05
\]

*Note 1:* If the \( \text{SO}_2 \text{(aq)} \) is oxidized to \( \text{SO}_4 \text{(aq)} \), the pH will be even lower since the resulting sulfuric acid (\( \text{H}_2\text{SO}_4 \)) is stronger than sulfurous acid (\( \text{H}_2\text{SO}_3 \)). See further the \( K_{a1} \) and \( K_{a2} \) values for \( \text{H}_2\text{SO}_4 \).

*Note 2:* A much lower pH results from a smaller amount of \( \text{SO}_2 \) than for \( \text{CO}_2 \). This is the result of two factors \( K_H(\text{SO}_2) \) is larger and \( K_{a1}(\text{SO}_2) \) is larger.

*Note 3:* If we consider the second dissociation using the \( K_{a2} \) expression, we solve for an additional \([\text{H}^+] = (K_{a2} \times [\text{HSO}_3^-])^{1/2} = 1.7 \times 10^{-7} \text{ M}\), which makes a relatively insignificant contribution to the pH when added to the \( 8.85 \times 10^{-5} \text{ M} \) already present from the first dissociation, \([\text{H}^+] \sim 8.85 \times 10^{-5} + 1.7 \times 10^{-7} = 8.86 \times 10^{-5} \text{ M} \).
4. Methane and carbon dioxide are produced under anaerobic conditions by the fermentation of organic matter, approximated by the following equation

\[ 2 \text{CH}_2\text{O} \rightarrow \text{CH}_4 + \text{CO}_2 \]

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 CH₄ and CO₂. We can then use the partial pressure of CH₄ inside the gas bubble and the corresponding Henry’s law constant to calculate the concentration of aqueous CH₄ 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 presence at appreciable concentrations and they are produced with 1:1 stoichiometry).

In order to ‘solve’ this problem, we need or calculate \( K_H \) for CH₄ 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.

\[
\ln \left( \frac{K_{T_2}}{K_{T_1}} \right) = \frac{H^\text{o}_{\text{rxn}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

where \( T_1 = 298\text{K}, T_2 = 278\text{K}, K_{T1} = 1.4 \times 10^{-8} \text{ M Pa}^{-1}, R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}, \Delta H^\text{o}_{\text{rxn}} = \text{enthalpy change for the aqueous dissolution of methane at std state conditions and } K_{T2} = \text{Henry’s law constant for methane at 278K.} \)

\[ \text{CH}_4(g) \rightleftharpoons \text{CH}_4(aq) \]

\[ \Delta H^\text{o}_{\text{rxn}} = [\Delta H^\text{o}_f (\text{CH}_4(aq))] - [\Delta H^\text{o}_f (\text{CH}_4(g))] = (-89.04 \text{ kJ mol}^{-1}) - (-74.80 \text{ kJ mol}^{-1}) = -14.24 \text{ kJ mol}^{-1} \text{ (Water Chemistry, M. Benjamin, Appendix A1, p635)} \]
Therefore,

\[ \ln \frac{K_{T2}}{K_{T1}} = 0.4135 \]

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, 2000. When the pollutant’s concentration reaches 90% of its steady state value, the flow of pollutant into the lake is stopped altogether. 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.

\[ \frac{[C]_t}{[C]_\infty} = 1 - e^{-kt} \]

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

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

\[ t_1 = \frac{-\ln (0.10)}{-0.35 \text{ yr}^{-1}} = \frac{-2.30}{-0.35 \text{ yr}^{-1}} = 6.58 \text{ yr} \]
\[ \frac{[C]_t}{[C]_0} = e^{-kt} \]

\[ \frac{(0.01)(0.90e^{7.60})}{(0.90 e^{7.60})} = e^{-kt} \]

\[ \ln(0.01) = -kt \]

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

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

\[ \text{Total time} = 6.58 + 13.16 \text{ yr} = 19.73 \text{ yrs} \]

\[ \text{July 1, 2019} + 266 \text{ days} \]

\[ \downarrow \]

\[ \text{Mar 23, 2020} \]
6. Derive an expression for the concentration of calcium as a function of $[\text{H}^+]$ and $P_{\text{CO}_2}$ for a water sample in equilibrium with atmospheric $\text{CO}_2(\text{g})$ and limestone ($\text{CaCO}_3$).

$$\text{CaCO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^{-}$$

Using Excel, plot the following graphs;

i) $[\text{Ca}^{2+}]$ as a function of $P_{\text{CO}_2}$ (0 – 0.0001 atm) at a constant $\text{pH} = 7.00$

ii) $[\text{Ca}^{2+}]$ as a function of $\text{pH}$ (4 – 10) at a constant $P_{\text{CO}_2} = 4.0 \times 10^{-4}$ atm

**Strategy:** The solubility of $\text{CaCO}_3(\text{s})$ will be given by the concentration of $\text{Ca}^{2+}$ 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 $\text{HCO}_3^{-}$, we can rearrange the expression and calculate the $[\text{Ca}^{2+}]$. Alternatively, we can write the solubility product expression for $\text{CaCO}_3$ 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 $[\text{H}^+]$.

**Solution:**

The solubility of calcium carbonate and thus the concentration of $\text{Ca}^{2+}$, will vary with changes in the $P_{\text{CO}_2}$ and $[\text{H}^+]$. To derive an expression for the $[\text{Ca}^{2+}]$ as a function of $P_{\text{CO}_2}$, we must first determine the $[\text{H}^+]$.

Rearranging the $K_{\text{sp}}$ expression for $\text{CaCO}_3$, we can write;

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

Remembering that we wish to express the $[\text{Ca}^{2+}]$ in terms of $P_{\text{CO}_2}$ and $[\text{H}^+]$, we look for an appropriate substitution for $[\text{CO}_3^{2-}]$.

Rearranging the $K_{a2}$ expression gives;

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

and we can substitute for $[\text{HCO}_3^{-}]$ using the $K_{a1}$ expression;

$$[\text{HCO}_3^{-}] = \frac{[\text{K}_{a1} [\text{CO}_2(\text{aq})] / [\text{H}^+]]}{[\text{H}^+]}$$

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

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

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

$$[\text{Ca}^{2+}] = \frac{K_{\text{sp}} [\text{H}^+]^2}{K_{a2} K_{a1} K_H P_{\text{CO}_2}}$$

From this expression we can see that the concentration of calcium depends not only on the $P_{\text{CO}_2}$, but also on the equilibrium concentration of $[\text{H}^+]$ – which we know will also depend on the $P_{\text{CO}_2}$. 
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;

\[
2 \,[Ca^{2+}] \, = \, [HCO_3^-]
\]

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 \(P_{CO2}\) (as before), yields;

\[
[Ca^{2+}] \, = \, \frac{K_{a1}K_HP_{CO2}}{2[H^+]}\]

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;

\[
\frac{K_{sp}[H^+]^2}{K_{a1}K_{a2}K_HP_{CO2}} \, = \, \frac{K_{a1}K_HP_{CO2}}{2[H^+]}\]

Rearranging and solving for \([H^+]\) yields;

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

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

and

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

Using Excel, let’s plot
i) \([Ca^{2+}]\) as a function of \(P_{CO2}\) (0 – 0.0001 atm) at a constant \(pH = 7.00\)
ii) $[\text{Ca}^{2+}]$ as a function of pH (4 – 10) at a constant $P_{\text{CO}_2} = 4.0 \times 10^{-4}$ atm

Note: Neither of these plots look like the one we saw in class for $[\text{Ca}^{2+}]$ vs $P_{\text{CO}_2}$ (Figure 11.2, textbook). This is because the solubility of CaCO$_3$ depends on both $[H^+]$ and $P_{\text{CO}_2}$ and the $[H^+]$ itself is dependent on $P_{\text{CO}_2}$. In other words, when the $P_{\text{CO}_2}$ increases, the $[H^+]$ also increases. How the $[\text{Ca}^{2+}]$ varies with $P_{\text{CO}_2}$, will depend on which effect is greater, in this case the $[H^+]$. 

![Equilibrium $[\text{Ca}^{2+}]$ as function of pH at $P_{\text{CO}_2}=0.0004$ atm](image1)

![Equilibrium $[\text{Ca}^{2+}]$ as function of $P_{\text{CO}_2}$](image2)
7. 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. Use a spreadsheet program (such as Excel) for repetitive calculations and to plot curves for fractional abundance of each species. What is the distribution of aluminum species at pH 5?

\[
pK_{a1} = 5.00 \quad pK_{a2} = 5.10 \quad pK_{a3} = 6.80 \quad pK_{a4} = 5.80
\]
8. 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 (mg/L \( O_2 \)) and DOC (mg/L C). Will your result change markedly using the generic formula for dissolved humic material (Fig 12.3, textbook)?

\[
\{CH_2O\} + O_2 \rightarrow CO_2 + H_2O
\]

\[
\text{mass } O_2 \text{ consumed} = \text{# mol/s } O_2 \text{ consumed} \times 32,000 \text{ mg mol}^{-1}
\]

\[
\text{# mol/s } O_2 \text{ consumed} = \text{# mol/s } CH_2O \text{ consumed}
\]

If \( \text{DOC} = 1.0 \text{ mg C L}^{-1} \), then we have

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

and \( 8.3 \times 10^{-5} \text{ mol CH}_2O \text{ L}^{-1} \)

so mass of \( O_2 \) consumed by \( 1.0 \text{ mg DOC} \text{ L}^{-1} \)

\[
8.3 \times 10^{-5} \text{ mol L}^{-1} \times 32,000 \frac{\text{mg}}{\text{mol}} = 2.7 \text{ mg L}^{-1}
\]

Therefore, \( 1.0 \text{ mg DOC L}^{-1} = 2.7 \text{ mg } O_2 \text{ L}^{-1} \), i.e. \( \text{COD} = 2.7 \text{ DOC} \)
9. Given the equilibria below, calculate the fractional abundance of Pb$^{2+}$ at pH 7.

\[ \text{Pb}^{2+} + \text{OH}^- \rightleftharpoons \text{PbOH}^+ \quad K = 2.0 \times 10^6 \]
\[ \text{PbOH}^+ + \text{OH}^- \rightleftharpoons \text{Pb(OH)}_2^- \quad K = 4.0 \times 10^4 \]

**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 our 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:**
\[
\text{Pb}^{2+} = \frac{[\text{Pb}^{2+}]}{[\text{Pb}^{2+}] + [\text{PbOH}^+] + [\text{Pb(OH)}_2^-]} 
\]

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

\[
\begin{align*}
\text{Pb}^{2+} + \text{OH}^- & \rightleftharpoons \text{PbOH}^+ & K_{f1} = 2.0 \times 10^6 \\
\text{H}_2\text{O} & \rightleftharpoons \text{H}^+ + \text{OH}^- & K_w = 1.0 \times 10^{-14} \\
\text{Pb}^{2+} + \text{H}_2\text{O} & \rightleftharpoons \text{PbOH}^+ + \text{H}^+ & K_{a1} = K_{f1} \times K_w = 2.0 \times 10^{-8} \\
\text{PbOH}^+ + \text{OH}^- & \rightleftharpoons \text{Pb(OH)}_2^- & K_{f2} = 4.0 \times 10^4 \\
\text{H}_2\text{O} & \rightleftharpoons \text{H}^+ + \text{OH}^- & K_w = 1.0 \times 10^{-14} \\
\text{PbOH}^+ + \text{H}_2\text{O} & \rightleftharpoons \text{Pb(OH)}_2^- + \text{H}^+ & K_{a2} = K_{f2} \times K_w = 4.0 \times 10^{-10}
\end{align*}
\]

Therefore, \( pK_{a1} = 7.7 \) and \( pK_{a2} = 9.4 \)

Given the magnitude of the \( pK_a \) 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;

\[
\text{Pb}^{2+} = \frac{[\text{Pb}^{2+}]}{[\text{Pb}^{2+}] + [\text{PbOH}^+]} 
\]

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

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

Hence at pH = 7, the fractional abundance of Pb$^{2+} = 0.833$
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 text and the conditional formation constant between Fe$^{2+}$ and fulvic acid of $5 \times 10^3$ 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.

\[
[\text{Fe}]_T = \frac{20 \text{ mg}}{\text{L}} \times \frac{1 \text{ mol}}{55.8 \text{ g}} \times \frac{1 \text{ g}}{10^3 \text{ mg}} = 3.58 \times 10^{-4} \text{ mol/L}
\]

\[
[\text{FAco}_2^-]_T = \frac{50 \text{ mg}}{\text{L}} \times \frac{4.5 \text{ mmol}}{9 \text{ DOM}} \times \frac{1 \text{ g}}{10^3 \text{ mg}} \times \frac{1 \text{ mol}}{10^3 \text{ mmol}}
\]

\[
= 2.25 \times 10^{-4} \text{ mol/L}
\]

\[
\text{Fe}^{2+} + \text{FAco}_2^- (aq) \rightleftharpoons \text{Fe-FAco}_2^- (aq)
\]

\[
K = \frac{[\text{Fe-FA}]}{[\text{Fe}]_f [\text{FAco}_2^-]_f} = 5 \times 10^3
\]

\[
[\text{Fe}]_T = [\text{Fe}]_f + [\text{Fe-FA}]
\]

\[
\therefore [\text{Fe}]_f = [\text{Fe}]_T - [\text{Fe-FA}]
\]

\[
[\text{FAco}_2^-]_T = [\text{FAco}_2^-]_f + [\text{Fe-FA}]
\]

\[
\therefore [\text{FAco}_2^-]_f = [\text{FAco}_2^-]_T - [\text{Fe-FA}]
\]
let \( x \) represent the concentration of ion complexed to fulvic acid

\[
x = [\text{Fe-FA}]
\]

So

\[
K = \frac{x}{([\text{Fe}^3_\text{T}] - x)([\text{FA}_{\text{CO}_2}] - x)} = 5 \times 10^3
\]

\[
= \frac{x}{(3.58 \times 10^{-4} - x)(2.25 \times 10^{-4} - x)} = 5 \times 10^3
\]

\[
= \frac{x}{8.06 \times 10^{-8} - 5.83 \times 10^{-4} x + x^2} = 5 \times 10^3
\]

\[
\therefore \quad x = 4.03 \times 10^{-4} - 2.91 x + 5000 x^2
\]

\[
0 = 4.03 \times 10^{-4} - 3.91 x + 5000 x^2
\]

\[
\begin{align*}
\therefore \quad x &= -b \pm \sqrt{b^2 - 4ac} \\
&= \frac{-3.91 \pm \sqrt{(3.91)^2 - 4(4.03 \times 10^{-4})(5000)}}{2(5000)} \\
&= \frac{3.91 \pm \sqrt{15.3 - 8.06}}{10,000}
\end{align*}
\]
Therefore,

\[ x = 6.6 \times 10^{-4} \text{ mol/L} \]

or

\[ x = 1.2 \times 10^{-4} \text{ mol/L} \]

Since the first solution for \( x \) is greater than the total Fe conc, it cannot be correct.

\[ [\text{Fe-FA}] = 1.2 \times 10^{-4} \text{ mol/L} \]

Fraction complexed is given by

\[ \frac{[\text{Fe-FA}]}{[\text{Fe}]} = \frac{1.2 \times 10^{-4}}{3.58 \times 10^{-4}} = 0.33 \text{ or 33\% complexed} \]

The complexation of \( \text{Fe}^{2+} \) with fulvic acid is known to be pH dependent. In general, there will be more complexation sites on fulvic acid as pH \( \uparrow \). Therefore, we expect more complexation of \( \text{Fe}^{2+} \) at pH 7 than pH 5.
11. What fraction of NTA (H₃T) is uncomplexed after H₂T° has been brought to equilibrium with solid PbCO₃ in an aqueous solution containing 1.25 mM HCO₃⁻ at pH 7.

\[
PbCO₃(s) + HT²⁻ \rightleftharpoons PbT⁻ + HCO₃⁻
\]

\[
\log K_{sp}(PbCO₃) = -13.13
\]

\[
\log K_f PbT⁻ = 11.34
\]

**Strategy:**
We want to solve for the fraction of NTA uncomplexed, which can be represented as the fraction \([HT²⁻]/([HT²⁻]+[PbT⁻])).  Let’s write out an equilibrium expression for the reaction given and and solve for \([HT²⁻]/[PbT⁻]).  If we can calculate the value of Keq from the information provided, we should be able to solve this one.

**Solution:**

\[
\frac{[HT²⁻]}{[HT²⁻]+[PbT⁻]} = \frac{K_{eq}[PbT⁻][HCO₃⁻]}{[HT²⁻]}
\]

Rearranging the equilibrium expression yields

\[
\frac{[PbT⁻]}{[HT²⁻]} \frac{K_{eq}}{[HCO₃⁻]}
\]

Substituting this into the fractional abundance expression yields

\[
\frac{[HT²⁻]}{[HT²⁻]+[HT²⁻]} = \frac{1}{1+\frac{K_{eq}[HCO₃⁻]}{[HCO₃⁻]}}
\]

Since \([HCO₃⁻] = 1.25 \times 10^{-3} \text{ M}\), all we need to solve this problem is the value of \(K_{eq}\).

Reducing the given equilibria to a series of simpler ones for which the equilibrium constants are known yields;

\[
\begin{align*}
PbCO₃(s) & \rightleftharpoons Pb^{2+} + CO₃^{2-} & \log K_{sp} = -13.13 \\
Pb^{2+} + T³⁻ & \rightleftharpoons PbT⁻ & \log K_f = 11.34 \\
HT²⁻ & \rightleftharpoons H^+ + T³⁻ & \log K_{a3} = -10.28 \\
CO₃^{2-} + H^+ & \rightleftharpoons HCO₃⁻ & \log(1/K_{a2}) = 10.33 \\
PbCO₃(s) + HT²⁻ & \rightleftharpoons PbT⁻ + HCO₃⁻ & \log K_{eq} = -1.74
\end{align*}
\]

So, \(K_{eq} = 1.82 \times 10^{-2}\) and

\[
\frac{1}{1+\frac{1.82 \times 10^{-2}}{1.25 \times 10^{-3}}} = 0.064
\]

Therefore, 6.4% of NTA is uncomplexed to Pb²⁺.
12. Kelthane is an agricultural pollutant that degrades with pseudo first order kinetics to dichlorobenzophenone (DCBP). Since Kelthane is difficult to measure, you decide instead to monitor the production of DCBP over time and obtain the following data. What is the half-life of Kelthane in this experiment?

<table>
<thead>
<tr>
<th>Time (weeks)</th>
<th>6</th>
<th>9</th>
<th>12</th>
<th>14</th>
<th>18</th>
<th>22</th>
<th>26</th>
<th>30</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc (ppm)</td>
<td>19</td>
<td>26</td>
<td>32</td>
<td>36</td>
<td>41</td>
<td>45</td>
<td>48</td>
<td>50</td>
<td>58</td>
</tr>
</tbody>
</table>

Strategy:
To calculate the half-life for Kelthane (a relationship between concentrations and time), we will need to use the integrated form of the first order rate equation. If we can determine $k$ (the rate constant) from the given data, we can use it to calculate $t_{1/2}$.

There are several ways to approach this. If we assume that each molecule of Kelthane yields one DCBP, we can write:

$$[\text{Kelthane}]_t = [\text{DCBP}]_{\text{inf}} - [\text{DCBP}]_t$$

where $[\text{DCBP}]_{\text{inf}}$ is taken as the conc once the reaction is complete at 150 weeks.

A plot of $\ln[\text{Kelthane}]$ vs time will yield a straight line with slope $= -k$

Solution:

<table>
<thead>
<tr>
<th>time weeks</th>
<th>[DCBP]_t</th>
<th>[Kel]_t</th>
<th>[Kel]_t/[Kel]_o</th>
<th>ln [Kel]</th>
<th>ln [Kel]_t/[Kel]_o</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>19</td>
<td>39</td>
<td>0.67</td>
<td>3.7</td>
<td>-0.40</td>
</tr>
<tr>
<td>9</td>
<td>26</td>
<td>32</td>
<td>0.55</td>
<td>3.5</td>
<td>-0.59</td>
</tr>
<tr>
<td>12</td>
<td>32</td>
<td>26</td>
<td>0.45</td>
<td>3.3</td>
<td>-0.80</td>
</tr>
<tr>
<td>14</td>
<td>36</td>
<td>22</td>
<td>0.38</td>
<td>3.1</td>
<td>-0.97</td>
</tr>
<tr>
<td>18</td>
<td>41</td>
<td>17</td>
<td>0.29</td>
<td>2.8</td>
<td>-1.23</td>
</tr>
<tr>
<td>22</td>
<td>45</td>
<td>13</td>
<td>0.22</td>
<td>2.6</td>
<td>-1.50</td>
</tr>
<tr>
<td>26</td>
<td>48</td>
<td>10</td>
<td>0.17</td>
<td>2.3</td>
<td>-1.76</td>
</tr>
<tr>
<td>30</td>
<td>50</td>
<td>8</td>
<td>0.14</td>
<td>2.1</td>
<td>-1.98</td>
</tr>
<tr>
<td>150</td>
<td>58</td>
<td>0</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
So $k = 0.0668 \text{ weeks}^{-1}$

and

$$\ln \frac{[\text{Kel}]}{[\text{Kel}_o]} = kt$$

at $t = t_{1/2}$, $[\text{Kel}]_t = \frac{1}{2} [\text{Kel}]_o$.

so

$$t_{1/2} = \ln 2 / k = (0.693/0.0668 \text{ weeks}^{-1}) = 10 \text{ weeks} !$$