

CHEM 301 Assignment #4

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

Due date: December 6th.

Only even numbered questions will be assessed.

1. Using information provided in your textbook, calculate the value of the p_e and pH for the 'triple point' between **HOCl/OCl⁻/Cl⁻**. Is hypochlorous acid thermodynamically stable at ambient conditions in freshwaters?

Solution: There are three boundaries that intersect at this point.

They relate to the following equilibria/half-reactions;

Acid/base (HOCl/OCl⁻)



Redox (HOCl/Cl⁻)



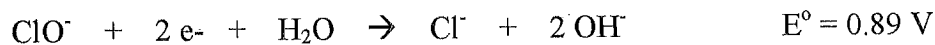
Redox (OCl⁻/Cl⁻)



The vertical boundary between HOCl and OCl⁻ occurs at $pH = pK_a = 7.52$

To determine the p_e value at the intersection, we will need the equation for either redox boundary in the form of $p_e = m pH + b$ and solve for the p_e at $pH = 7.52$

Appendix B5 (vanLoon) has the following half-reaction

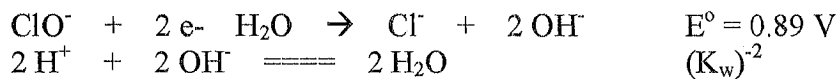


This is a start, but it is not in a convenient form if we want to use,

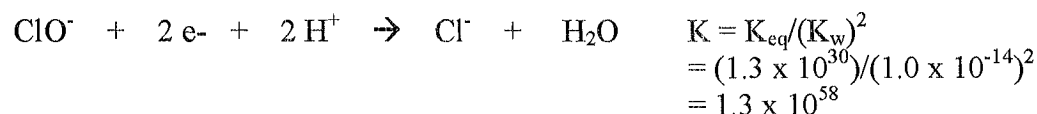
$$p_e = p_e^\circ - (n_H/n_e) pH - (1/n_e) \log \{\text{red}\}/\{\text{oxid}\}$$

where we need the number of mols of H⁺ in the half-reaction.

One approach of addressing this is as follows;



Since we can write $K_{\text{eq}} = e^{\{nFE^\circ/RT\}} = 1.3 \times 10^{30}$
 (recall for any redox reaction, $\Delta G^\circ = -nFE^\circ$ and $\Delta G^\circ/RT = \ln K_{\text{eq}}$),
 we can add these reactions and calculate an new equilibrium constant (K) for the reaction
 below.



Converting this back to an E° value yields;

$$E^\circ = (RT/nF) \ln K = 1.72 \text{ V}$$

$$\text{Since } pe^\circ = E^\circ/0.0592 = 29.0,$$

We can write the equation for the boundary condition as

$$pe = 29.0 - pH - \frac{1}{2} \log \left\{ \frac{\text{ClO}^-}{\text{Cl}^-} \right\}$$

and therefore the pe at the intersection of HOCl/OCl⁻/Cl⁻ is given by

$$pe = pe^\circ - 7.52 = 29.0 - 7.52 = 21.5$$

This is more or less consistent with the $pe - pH$ diagram given below.

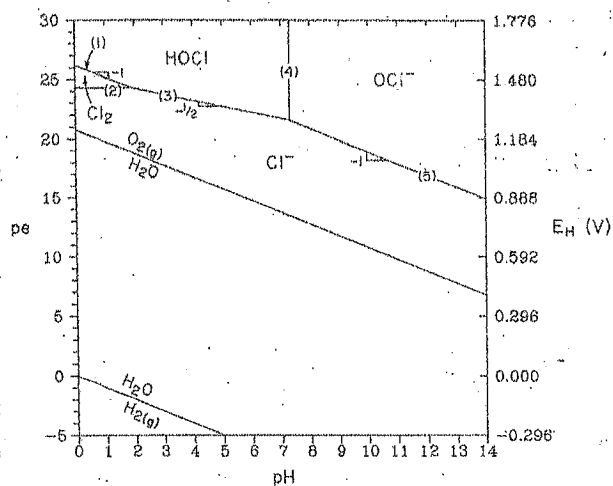


Figure 20.3 pe - pH predominance diagram for aqueous chlorine at $25^\circ\text{C}/1$ atm and $\text{Cl}_T = 0.04 \text{ M}$. The criterion for each boundary line is that there be equal mass amounts of chlorine present for both-species along the line. This assumption leads to a contradiction at the intersection of lines 1 and 2. In actuality, the Cl_2 is not a sharp wedge as shown here, but a blunt wedge.

Neither HOCl or OCl⁻ is thermodynamically stable in water.

2. A drinking water treatment facility uses a one million liter flow through chlorination tank and requires a 30 min contact time (residence time) for dis-infection.
- How many liters of water can be treated per hr using this system?
 - How much chlorine (mass in kg as Cl_2) will be used in one day, if the source water has a chlorine demand of 0.40 ppm and the finished water is to have a chlorine residual of 1.0 ppm?

Solution:

- Use the definition of residence time to solve this one.

Residence time = stock/flux

$$\therefore \text{flux} = \text{stock}/\text{residence time} = 1.0 \times 10^6 \text{ L}/(0.5 \text{ hr}) = \mathbf{2.0 \times 10^6 \text{ L/hr}}$$

- The amount of chlorine required (dose) = demand + residual

$$= 1.0 + 0.4 \text{ ppm Cl}_2 = 1.4 \text{ ppm Cl}_2 = 1.4 \text{ mg Cl}_2/\text{L}$$

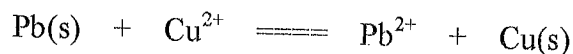
$$\text{Since the volume of water treated per day} = 2.0 \times 10^6 \text{ L/hr} \times 24 \text{ hr/day} = 4.8 \times 10^7 \text{ L/day}$$

$$\therefore \text{total Cl}_2 \text{ required per day} = 1.4 \text{ mg/L} \times 4.8 \times 10^7 \text{ L/day} = 6.7 \times 10^7 \text{ mg/day}$$

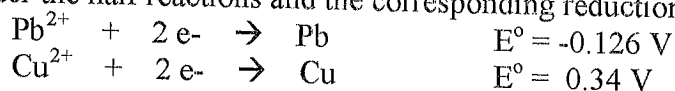
or **67 kg Cl_2 per day**

3. Lead solder on copper plumbing has been suggested as a possible source of low levels of lead (II) ions in drinking water. Using the standard reduction tables and the Nernst equation, comment on the possibility of Pb^{2+} being present at or above the MAC of 10. ppb, if the water in contact with $\text{Pb}(s)$ contains Cu^{2+} at 0.10 ppm (*ignore Cu^+ ions*).

Solution: The relevant chemical reaction is;



Consider the half reactions and the corresponding reduction potentials,



Therefore, at standard state (i.e., $[\text{Pb}^{2+}] = [\text{Cu}^{2+}] = 1.0 \text{ M}$), $E^\circ = 0.466 \text{ V}$

Since when $E^\circ > 0$, $\Delta G^\circ < 0$ and the reaction is SPONTANEOUS in the direction written.

To determine if this reaction is still spontaneous with the concentrations given in the question, we need to apply the Nernst equation.

$$E = E^\circ - \frac{2.3RT}{nF} \log Q$$

where $Q = [\text{Pb}^{2+}]/[\text{Cu}^{2+}]$

Converting the given concentration and substituting into the Nernst equation.

$$\begin{array}{l} [\text{Pb}^{2+}] = 10. \text{ ug/L} \times 1 \text{ mol}/(207 \times 10^6 \text{ ug}) = 4.8 \times 10^{-8} \text{ mol/L} \\ [\text{Cu}^{2+}] = 0.10 \text{ mg/L} \times 1 \text{ mol}/(63.5 \times 10^3 \text{ mg}) = 1.6 \times 10^{-6} \text{ mol/L} \end{array}$$

$$E = E^\circ - \frac{2.3RT}{nF} \log Q = 0.466 \text{ V} - \frac{2.3(8.314 \text{ Jmol}^{-1} \text{ K}^{-1})(298 \text{ K})}{2(96485 \text{ Cmol})} \log \frac{4.8 \times 10^{-8}}{1.6 \times 10^{-6}} = 0.506 \text{ V}$$

Therefore under the reaction conditions given, we can see that the release of Pb^{2+} at levels that meet or exceed the MAC is quite feasible.

4. Filter alum $\text{Al}_2(\text{SO}_4)_3$ is often used to remove phosphate from wastewater. A wastewater with a pH = 5.62 containing 25 ppm total phosphate is treated with alum until the equilibrium concentration of Al^{3+} is $4.0 \times 10^{-9} \text{ mol L}^{-1}$. What fraction of the total phosphate is precipitated as $\text{AlPO}_4(\text{s})$? Consider that the phosphate ion concentration is controlled by the precipitation of aluminum phosphate ($K_{\text{sp}} = 1.0 \times 10^{-21}$) and ignore the precipitation of $\text{Al}(\text{OH})_3$.

Solution: The goal here is to calculate the fraction of phosphorous removed by precipitation with alum treatment.



We can define this fraction as;

$$\text{fraction removed} = \frac{[\text{PO}_4]_{\text{T}}^{\text{removed}}}{[\text{PO}_4]_{\text{T}}^{\text{initial}}} = \frac{[\text{PO}_4]_{\text{T}}^{\text{initial}} - [\text{PO}_4]_{\text{T}}^{\text{final}}}{[\text{PO}_4]_{\text{T}}^{\text{initial}}}$$

$$[\text{PO}_4]_{\text{T}}^{\text{initial}} = 25 \text{ mg PO}_4/\text{L} \times 1 \text{ mol}/95,000 \text{ mg} = 2.6 \times 10^{-4} \text{ M}$$

present as $[\text{H}_3\text{PO}_4]$, $[\text{H}_2\text{PO}_4^-]$, $[\text{HPO}_4^{2-}]$, and $[\text{PO}_4^{3-}]$ depending on the pH

At pH = 5.62 ($[\text{H}^+] = 10^{-5.62} = 2.4 \times 10^{-6} \text{ M}$), we will recognize that most of the phosphate ion will be H_2PO_4^- based on the values of $K_{\text{a}1}$, $K_{\text{a}2}$ and $K_{\text{a}3}$ for phosphoric acid. While the H_3PO_4 and PO_4^{3-} forms will contribute relatively little to the total phosphate, we can ignore the contribution of H_3PO_4 but the PO_4^{3-} is relevant since it will control the total phosphate concentration via precipitation as AlPO_4 .

We can calculate the $[\text{PO}_4]_{\text{T}}^{\text{final}}$ using the equilibrium concentration of PO_4^{3-} (from the K_{sp} expression) and the pH to account for the various forms of orthophosphate (i.e., $\text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}/\text{PO}_4^{3-}$) as follows.



Rearranging the K_{sp} expression gives;

$$[\text{PO}_4^{3-}] = K_{\text{sp}}/[\text{Al}^{3+}] = 1.0 \times 10^{-21}/4.0 \times 10^{-9} = 2.5 \times 10^{-13} \text{ M}$$

Rearranging the $K_{\text{a}3}$ expression yields;

$$[\text{HPO}_4^{2-}] = [\text{PO}_4^{3-}] [\text{H}^+]/K_{\text{a}3} = (2.5 \times 10^{-13}) (2.4 \times 10^{-6})/4.2 \times 10^{-13} = 1.4 \times 10^{-6} \text{ M}$$

$$\text{similarly for } [\text{H}_2\text{PO}_4^-] = [\text{HPO}_4^{2-}] [\text{H}^+]/K_{\text{a}2} = (1.4 \times 10^{-6}) (2.4 \times 10^{-6})/6.3 \times 10^{-8} = 5.3 \times 10^{-5} \text{ M}$$

Therefore, the $[\text{PO}_4^{3-}]_{\text{T}}^{\text{final}} \sim$ equilibrium concentration of $[\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] = 5.4 \times 10^{-5} \text{ M}$

$$\text{So the fraction removed} = (2.6 \times 10^{-4} \text{ M} - 5.4 \times 10^{-5} \text{ M})/2.6 \times 10^{-4} \text{ M} = 0.80 \text{ (80\% removal)}$$

An alternative approach would be to consider the equilibrium



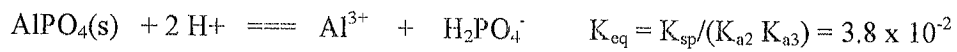
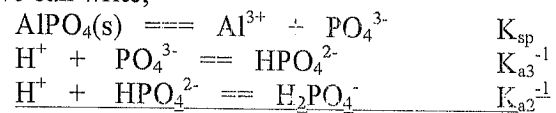
where we have employed the dominant form of phosphate at pH = 5.62.

The equilibrium expression is therefore $K_{\text{eq}} = [\text{Al}^{3+}] [\text{H}_2\text{PO}_4^-] / [\text{H}^+]^2$

Since we know the concentration of Al^{3+} and H^+ , we can solve for $[\text{H}_2\text{PO}_4^-]$, if we can calculate value for K_{eq} as follows;

$$[\text{H}_2\text{PO}_4^-] = K_{\text{eq}} [\text{H}^+]^2 / [\text{Al}^{3+}]$$

Since we can write,



Therefore, $[\text{H}_2\text{PO}_4^-] = 5.4 \times 10^{-5} \text{ M}$

And again we calculate $[\text{PO}_4^{3-}]_{\text{T}}^{\text{final}} \sim 5.4 \times 10^{-5} \text{ M}$ and 80% removal.

5. The Langelier index (LI) uses the difference between the actual pH of a solution and the calculated pH of a saturated solution to predict whether or not calcite scale

($\text{CaCO}_3(\text{s})$) will form, where $\text{LI} = \text{pH}_{\text{actual}} - \text{pH}_{\text{saturated}}$

If $\text{LI} > 0$, then water is supersaturated and calcite precipitation occurs. A water supply has the following reported water quality parameters. Predict the potential for scale formation based on the temperature dependence of K_{sp} (calcite) and K_{a2} (carbonic acid) given by the following empirical temperature regressions (Kelvin).

Temperature = 8 °C

pH = 7.89

Calcium Hardness = 178 ppm CaCO_3

Total Alkalinity = 120 ppm CaCO_3

$$\text{Log } K_{\text{sp}} = -171.9065 - 0.077993(T) + 2839.32(T)^{-1} + 71.595 (\log T)$$

$$\text{Log } K_{\text{a2}} = -107.887 - 0.0325285(T) + 5151.79(T)^{-1} + 38.9256 (\log T) - 563713.9 (T)^{-2}$$

Solution: The Langelier index requires knowledge of the $\text{pH}_{\text{actual}}$ (a measured value) and a calculated pH at saturation (pH_{sat}).

$$\text{LI} = \text{pH}_{\text{act}} - \text{pH}_{\text{sat}}$$

The pH_{sat} is given by the following expression (based on the pH dependence of the calcite solubility and rearranging the K_{sp} expression for $\text{CaCO}_3(\text{s})$, see notes);

$$\text{pH}_{\text{sat}} = \log K_{\text{sp}} - \log K_{\text{a2}}(\text{HCO}_3^-) - \log \{\text{Ca}^{2+}\} - \log \{\text{HCO}_3^-\}$$

The two equilibrium constants are temperature dependent and their values at 8°C are given as,

$$\log K_{\text{sp}} @ 8^\circ\text{C} = -8.404$$

$$\log K_{\text{a2}} @ 8^\circ\text{C} = -10.513$$

The molar concentrations of the calcium and bicarbonate ions are given by;

$$[\text{Ca}^{2+}] = 178 \text{ mg CaCO}_3/\text{L} \times 1 \text{ mol}/100,000 \text{ mg} = 1.78 \times 10^{-3} \text{ M}$$

$$[\text{HCO}_3^-] = 120 \text{ mg CaCO}_3/\text{L} \times 1 \text{ mol}/100,000 \text{ mg} \times 2 \text{ mol H}^+/1 \text{ mol CaCO}_3 \times 1 \text{ mol HCO}_3^-/1 \text{ mol H}^+ = 2.4 \times 10^{-3} \text{ M}$$

Assuming a dilute solution in which activities \approx molar concentrations and substituting the above values into the equation for pH_{sat} yields;

$$\text{pH}_{\text{sat}} = -8.404 - (-10.513) - \log (1.78 \times 10^{-3}) - \log (2.4 \times 10^{-3}) = 7.479$$

and therefore,

$$\text{LI} = 7.89 - 7.48 = 0.41, \text{ which is } > 0 \text{ and the solution is supersaturated.}$$

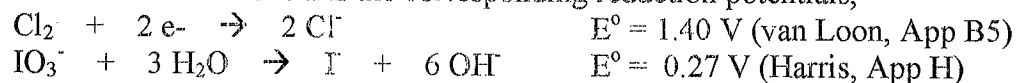
Therefore, calcite will form under these conditions.

6. One of the concerns of chlorine based dis-infection is the inadvertent oxidation of iodide to *active* iodine (and hypoiodous acid) and the subsequent reaction with dissolved organic carbon to form genotoxic iodinated dis-infection by-products. It turns out that under most natural water conditions chlorine will oxidize iodide ion to the less reactive iodate ion. However, chloramines (which are less powerful oxidants) have employed in place of chlorine (because of concerns over trichloromethane formation) will oxidize iodide ion to *active* iodine, which subsequently reacts with water to form hypoiodous acid. This active form of iodine has been observed to react further with DOC to yield iodinated trihalomethanes and haloacetic acids.

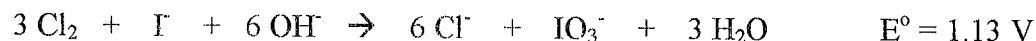
a) Use the standard reduction potentials of Cl_2 and IO_3^- to confirm that the oxidation of iodide ion to iodate is spontaneous under standard conditions.

b) Write a series of chemical reactions that outline the formation of an iodinated DBP when a natural water supply containing iodide ion and DOC is treated with chloroamine. (See further S. Krasner, *The formation and control of emerging disinfection by-products of health concern*, *Phil. Trans. R. Soc. A* (2009) 367, 4077–4095. doi:10.1098/rsta.2009.0108)

a) Consider the half reactions and the corresponding reduction potentials,

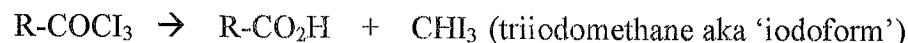
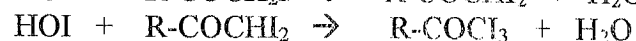
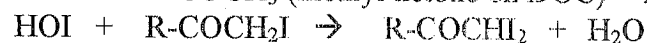
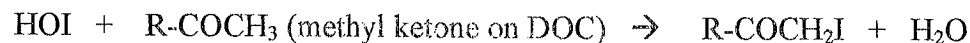


The overall redox process is therefore given by;

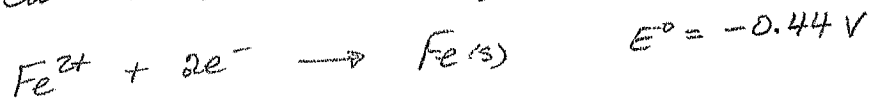
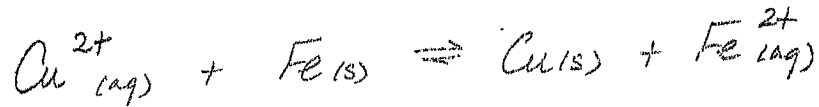


Since $E^\circ > 0$, the reaction is spontaneous at standard conditions

b) The formation of iodinated dis-infection by-products where ‘active iodine’ is incorporated into organic molecules requires the formation of hypoiodous acid and/or hypoiodite ion (HOI/OI^-). These are an intermediate oxidation state of iodine (+I) rather than the (+V) present in the iodate ion. Since chloramines ($\text{NH}_2\text{Cl}/\text{NHCl}_2/\text{NCl}_3$) are less powerful oxidizing agent (i.e., smaller E° values), they can oxidize I^- to HOI , thus producing the active iodine that reacts with dissolved organic carbon. An example reaction series is outlined below;



7. Calculate the maximum theoretical removal of copper from a leachate containing 145 ppm of Cu^{2+} with the use of zero valent iron by the 'cementation' reaction if cupric ion is the only cation present. Does your result change if the solution contains 350 ppm of Fe^{2+} .



$$\therefore \text{overall rxn} \quad E^\circ = 0.78 \text{ V} \quad (\text{std. state cond.})$$

$$\text{So } \Delta G^\circ_{\text{rxn}} = -nFE^\circ$$

$$= - (2)(96,480)(0.78)$$

$$= -150.5 \frac{\text{kJ}}{\text{mol}} \quad \text{when } [\text{Cu}^{2+}] = [\text{Fe}^{2+}] = 1 \text{ M}$$

$$\therefore K_{\text{eq}} = 10^{-\Delta G^\circ / 2.3RT} = 6.0 \times 10^{19} \quad (\text{i.e. favourable in direction written, above})$$

$$K_{\text{eq}} = \frac{[\text{Fe}^{2+}]}{[\text{Cu}^{2+}]} = 6.0 \times 10^{19}$$

\therefore essentially all of Cu^{2+} is removed from solution by $\text{Fe}(\text{s})$

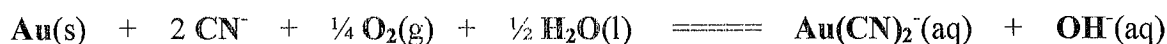
i.e., 145 mg Cu could be recovered per liter of water treated

The concentration of Cu^{2+} remaining in solution would be given by

$$[\text{Cu}^{2+}] = [\text{Fe}^{2+}] / K_{\text{eq}} = 6.3 \times 10^{-3} \text{ M} / 6.0 \times 10^{19} = 1 \times 10^{-22} \text{ M}$$

(i.e., it is still essentially completely removed from solution)

8. Gold ores are frequently leached with cyanide dissolving the gold according to;



Which has an equilibrium constant, $K = 1.2 \times 10^{17}$. In order to prevent undue environmental contamination by cyanide, you wish to operate this process under conditions such that at least 98% of the CN^- is converted to $\text{Au}(\text{CN})_2^-$. Your process operates at a pH 9.0 and the O_2 pressure inside the ore body is constant at 0.032 atm. Calculate the molar concentration of CN^- required.

$$K_{\text{eq}} = \frac{[\text{Au}(\text{CN})_2^-][\text{OH}^-]}{[\text{CN}^-]^2 P_{\text{O}_2}^{1/4}} = 1.2 \times 10^{17}$$

$\xrightarrow{10^{-5} \text{ M}}$
 $\xleftarrow{0.032 \text{ atm}}$

$$\text{also } 0.98 = \frac{[\text{Au}(\text{CN})_2^-]}{[\text{CN}^-]_{\text{T}}} = \frac{[\text{Au}(\text{CN})_2^-]}{[\text{Au}(\text{CN})_2^-] + [\text{CN}^-]}$$

from K_{eq} expression, we can write

$$[\text{CN}^-]^2 = \frac{[\text{Au}(\text{CN})_2^-][\text{OH}^-]}{K_{\text{eq}} \cdot P_{\text{O}_2}^{1/4}}$$

and rearranging the fractional abundance expression yields,

$$0.98 ([\text{Au}(\text{CN})_2^-] + [\text{CN}^-]) = [\text{Au}(\text{CN})_2^-]$$

$$\text{So, } 0.98 [\text{CN}^-] = 0.02 [\text{Au}(\text{CN})_2^-]$$

$$\text{and } [\text{Au}(\text{CN})_2^-] = \frac{0.98}{0.02} [\text{CN}^-] = 49 [\text{CN}^-]$$

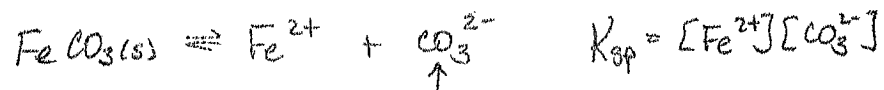
$$\therefore [\text{CN}^-]^2 = \frac{49 [\text{CN}^-][\text{OH}^-]}{K_{\text{eq}} \cdot P_{\text{O}_2}^{1/4}}$$

$$\text{and } [\text{CN}^-] = \frac{49 [\text{OH}^-]}{K_{\text{eq}} \cdot P_{\text{O}_2}^{1/4}} = \frac{(49)(10^{-5} \text{ M})}{(1.2 \times 10^{17})(0.032)^{1/4}} = \boxed{1 \times 10^{-20} \text{ M}}$$

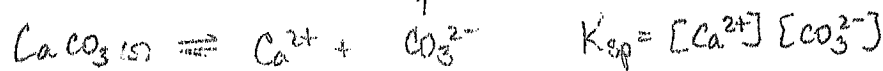
note: it takes very low equil. conc. of CN^- to affect 98% complexation.

9. Iron can occur as a carbonate mineral FeCO_3 , which has a $K_{sp} = 3.1 \times 10^{-11}$. Calculate the concentration of Fe^{2+} (ppm) in a groundwater in equilibrium with iron (II) carbonate, given that the concentration of calcium ion in equilibrium with solid calcium carbonate ($K_{sp} = 6.0 \times 10^{-9}$) is 120 ppm.

Solution: We can use the solubility of CaCO_3 to calculate the concentration the carbonate ion, which will then control the aqueous concentration of ferrous iron.



↑
common ion
from CaCO_3 dissolution



$$[\text{CO}_3^{2-}] = \frac{K_{sp}}{[\text{Ca}^{2+}]} = \frac{6.0 \times 10^{-9}}{\left(\frac{120 \text{ mg}}{\text{L}} \cdot \frac{1 \text{ mol}}{40,000 \text{ mg}} \right)}$$

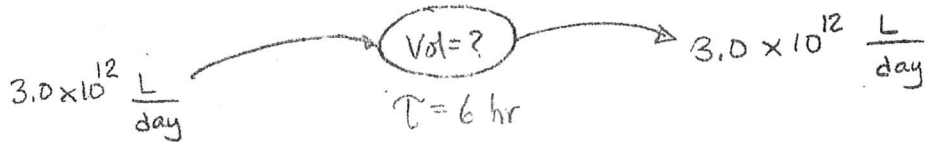
$$= 2.0 \times 10^{-6} \text{ M}$$

$$\therefore [\text{Fe}^{2+}] = \frac{K_{sp}}{[\text{CO}_3^{2-}]} = \frac{3.1 \times 10^{-11}}{2.0 \times 10^{-6}} = 1.6 \times 10^{-5} \text{ M}$$

converting

$$1.6 \times 10^{-5} \frac{\text{mol}}{\text{L}} \times \frac{55,800 \text{ mg}}{1 \text{ mol}} = \boxed{0.87 \text{ ppm}}$$

10. A sewage treatment plant is designed to process 3.0×10^{12} L of wastewater daily.
- a) What capacity (m^3) is required for the primary settling lagoon if the residence time is to be 6 hours?
- b) If the influent water has a BOD of 850 ppm, what volume (m^3) of air at $15^\circ C$ is required per hour to provide the oxygen to reduce the BOD by 90%.



$$\bar{T} = \frac{M}{F} \quad \therefore M = \bar{T} \cdot F$$

$$= 6 \text{ hr} \cdot 3.0 \times 10^{12} \frac{\text{L}}{\text{day}} \cdot \frac{1 \text{ day}}{24 \text{ hr}}$$

$$= 7.5 \times 10^{11} \text{ L} \quad \text{or} \quad 750 \times 10^6 \text{ m}^3$$

BOD = $850 \frac{\text{mg O}_2}{\text{L}}$; at 90% reduction BOD = $85 \frac{\text{mg O}_2}{\text{L}}$

$$\therefore 765 \frac{\text{mg O}_2}{\text{L}} \times 3.0 \times 10^{12} \frac{\text{L}}{\text{day}} \times \frac{1 \text{ mol}}{32,000 \text{ mg}} = 7.2 \times 10^{10} \text{ moles O}_2 / \text{day}$$

Since $PV = nRT$, $V = \frac{nRT}{P} = \frac{(7.2 \times 10^{10} \text{ moles})(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})(288 \text{ K})}{(1 \text{ atm})}$

$$V_{\text{O}_2} = 1.7 \times 10^{12} \text{ L of O}_2 / \text{d}$$

$$V_{\text{air}} = 1.7 \times 10^{12} \text{ L} \times \frac{1 \text{ L air}}{0.21 \text{ L O}_2} = 8.1 \times 10^{12} \text{ L air} / \text{d}$$

$$\therefore V_{\text{air}} = \frac{8.1 \times 10^{12} \text{ L}}{\text{d}} \times \frac{1 \text{ m}^3}{10^3 \text{ L}} \times \frac{1 \text{ d}}{24 \text{ hr}} = \frac{3.4 \times 10^8 \text{ m}^3}{\text{hr}}$$

↑
($\frac{\text{m}^3}{\text{hr}}$)