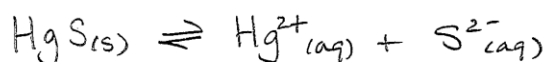


CHEM 301
Assignment #4 (Optional)

Provide solutions to the following questions in a neat and well organized manner.
Clearly state assumptions and reference sources for any constants used.
(odd numbered questions only) December 7th

1. The Maximum Acceptable Concentration of mercury in water is 0.001 ppm. Is the MAC likely to be exceeded by the dissolution of a) **HgS**(s) ($K_{sp} = 1 \times 10^{-56}$) and b) **HgO**(s) (solubility reported as 5.3 mg per 100 mL). Are either of your answers affected by the pH or pe of the water sample? Explain.

$$\text{MAC for Hg} = 0.001 \text{ ppm}$$



$$K_{sp} = [\text{Hg}^{2+}][\text{S}^{2-}] = 1 \times 10^{-56}$$

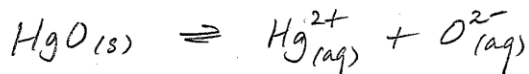
$$\text{if } [\text{Hg}^{2+}] = [\text{S}^{2-}]$$

$$\text{then } [\text{Hg}^{2+}]^2 = 1 \times 10^{-56}$$

$$\text{and } [\text{Hg}^{2+}] = 1 \times 10^{-28} \text{ M}$$

$$1 \times 10^{-28} \frac{\text{mol}}{\text{L}} \times \frac{200.6 \text{ g}}{1 \text{ mol}} \times \frac{10^3 \text{ mg}}{1 \text{ g}} = 2 \times 10^{-23} \frac{\text{mg}}{\text{L}}$$

NO!

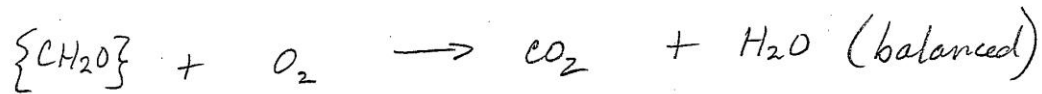


5.3 mg HgO dissolves in 100 mL water

$$\frac{5.3 \text{ mg HgO}}{0.1 \text{ L}} \times \frac{200.6 \text{ g/mol}}{216.6 \text{ g/mol}} = \frac{49 \text{ mg Hg}}{\text{L}}$$

YES!

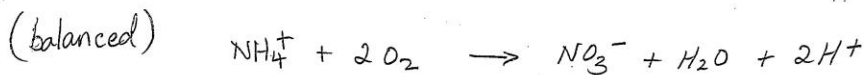
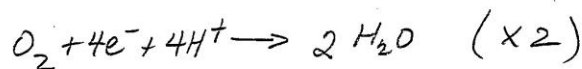
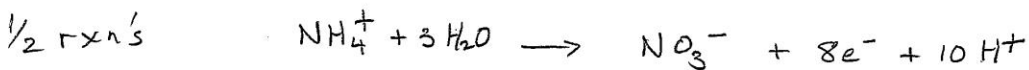
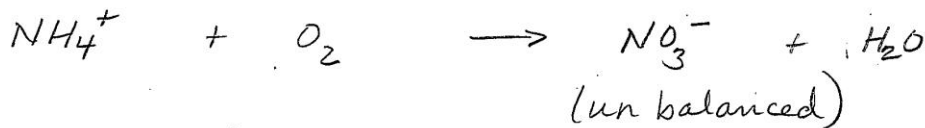
2. An effluent waste stream contains 330 mg L^{-1} organic matter (suspended and dissolved) and 27 mg L^{-1} ammonium ion (as N). Write chemical equations for the complete oxidation of $\{\text{CH}_2\text{O}\}$ and NH_4^+ and calculate the total BOD load of this effluent in mg/L O_2 .



$$330 \text{ mg/L of CH}_2\text{O} \times \frac{1 \text{ mol}}{30. \text{ g}} \times \frac{1. \text{ g}}{10^3 \text{ mg}} = 1.1 \times 10^{-2} \frac{\text{mol}}{\text{L}}$$

\therefore BOD from CH_2O

$$1.1 \times 10^{-2} \frac{\text{mol O}_2}{\text{L}} \times \frac{32,000 \text{ mg}}{1 \text{ mol O}_2} = 352 \frac{\text{mg O}_2}{\text{L}}$$



$$27 \frac{\text{mg N}}{\text{L}} \times \frac{1 \text{ mol}}{14. \text{ g}} \times \frac{1 \text{ g}}{10^3 \text{ mg}} = 1.9 \times 10^{-3} \frac{\text{mol}}{\text{L}}$$

\therefore BOD from NH_4^+

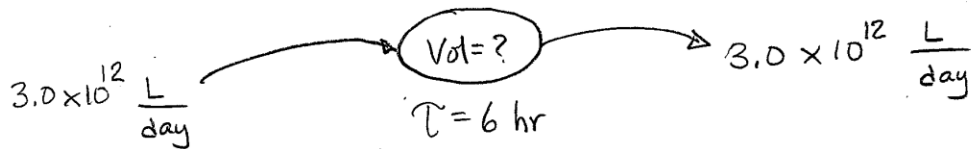
$$3.9 \times 10^{-3} \frac{\text{mol O}_2}{\text{L}} \times \frac{32,000 \text{ mg}}{1 \text{ mol O}_2} = 123 \frac{\text{mg O}_2}{\text{L}}$$

$$\text{Therefore total BOD} = 352 + 123 \frac{\text{mg O}_2}{\text{L}} = 475 \frac{\text{mg O}_2}{\text{L}}$$

3. A sewage treatment plant is designed to process 3.0×10^{12} L of sewage 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 of oxygen at 15°C is required per day to reduce the BOD by 90%.



$$\tau = \frac{M}{F}$$

$$\therefore M = \tau \cdot F$$

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

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

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

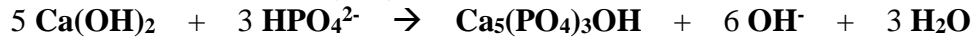
$$\therefore 765 \frac{\text{mg O}_2}{\text{L}} \times 3.0 \times 10^{12} \frac{\text{L}}{\text{day}} \times \frac{1 \text{ mol}}{32,000 \text{ mg}} = 7.2 \times 10^{10} \text{ mols O}_2$$

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

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

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

4. Calculate the mass of lime ($\text{Ca(OH)}_2(\text{s})$), required to chemically treat $27,000 \text{ m}^3$ of waste water containing 6.1 mg L^{-1} of phosphorous. Assume the following reaction goes to completion when a two fold molar excess of Ca(OH)_2 is used.



Strategy: Convert conc. phosphorus to mol/L and use stoichiometry to calculate mols Ca(OH)_2 required per litre. Multiply by volume and double for required excess. Convert to mass in final step.

Solution:

$$\text{mass Ca(OH)}_2 = n_{\text{Ca(OH)}_2} \times \text{MW}_{\text{Ca(OH)}_2} \times 2 \text{ (excess)}$$

↑
74.3/mol

$$n_{\text{Ca(OH)}_2} = n_{\text{HPO}_4^{2-}} \times \frac{5 \text{ mol Ca(OH)}_2}{3 \text{ mol HPO}_4^{2-}}$$

$$n_{\text{HPO}_4^{2-}} = 6.1 \frac{\text{mg}}{\text{L}} \times \frac{1 \text{ mol}}{31 \text{ g}} \times \frac{1 \text{ g}}{10^3 \text{ mg}} \times 27,000 \text{ m}^3 \times \frac{10^3 \text{ L}}{1 \text{ m}^3}$$

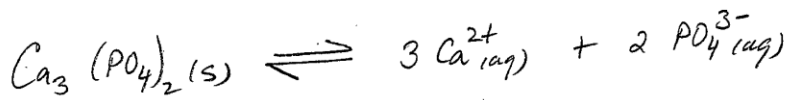
$$= 5.31 \times 10^3 \text{ mol H}_2\text{PO}_4^{2-}$$

$\therefore \text{mass Ca(OH)}_2 = 1310 \text{ kg}$

5. A sewage sample contains 8.8 ppm of dissolved phosphorous in the form of ortho phosphate. It is brought to pH of 9.0 and $[Ca^{2+}] = 4.7 \text{ mM}$ by the addition of $Ca(OH)_2$. What is the concentration of dissolved phosphorous (as ppm P) when it's in equilibrium with precipitated calcium phosphate ($K_{sp} Ca_3(PO_4)_2 = 1 \times 10^{-24}$)?

$$8.8 \frac{\text{mg P}}{\text{L}} \times \frac{1 \text{ mol}}{31.9} \times \frac{1 \text{ g}}{10^3 \text{ mg}} = 2.8 \times 10^{-4} \text{ M}$$

After addition of $Ca(OH)_2$, the PO_4^{3-} concentration is controlled by the solubility of $Ca_3(PO_4)_2(s)$.



$$K_{sp} = [Ca^{2+}]^3 [PO_4^{3-}]^2 = 1 \times 10^{-24}$$

At equilibrium, $pH = 9.0$ and $[Ca^{2+}] = 4.7 \times 10^{-3} \text{ M}$

$$[PO_4^{3-}] = \sqrt{\frac{K_{sp}}{[Ca^{2+}]^3}} = \left[\frac{1 \times 10^{-24}}{(4.7 \times 10^{-3})^3} \right]^{1/2} = 3.1 \times 10^{-9} \text{ M}$$

dissolved ortho phosphorus = $[PO_4]_T$

$$[PO_4]_T = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$$

↑
 ≈ 0 at pH 9

use

K_{a3} and K_{a2} to express $[HPO_4^{2-}]$ and $[H_2PO_4^-]$ in terms of $[PO_4^{3-}]$ and $[H^+]$

$$\text{from } K_{a3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.2 \times 10^{-13} \text{ (data sheet)}$$

$$\begin{aligned}\therefore [HPO_4^{2-}] &= \frac{[H^+][PO_4^{3-}]}{K_{a3}} \\ &= \frac{(10^{-9.0})(3.1 \times 10^{-9})}{4.2 \times 10^{-13}} \\ &= 7.4 \times 10^{-6} \text{ M}\end{aligned}$$

$$\text{from } K_{a2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.3 \times 10^{-8} \text{ (data sheet)}$$

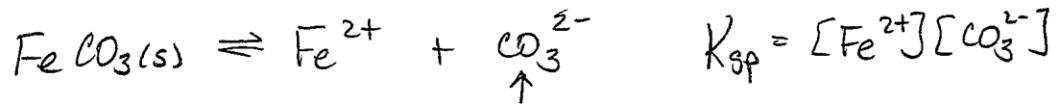
$$\begin{aligned}\therefore [H_2PO_4^-] &= \frac{[H^+][HPO_4^{2-}]}{K_{a2}} \\ &= \frac{(10^{-9.0})(7.4 \times 10^{-6})}{6.3 \times 10^{-8}} \\ &= 1.2 \times 10^{-7} \text{ M}\end{aligned}$$

$$\begin{aligned}\therefore [PO_4]_T &= 1.2 \times 10^{-7} \text{ M} + 7.4 \times 10^{-6} \text{ M} + 3.1 \times 10^{-9} \text{ M} \\ &= 7.5 \times 10^{-6} \text{ M}\end{aligned}$$

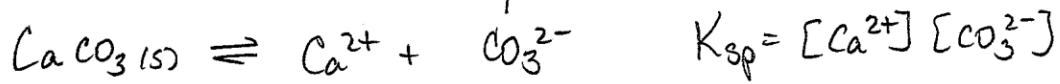
Converting to ppm P

$$7.5 \times 10^{-6} \frac{\text{mol } PO_4^{3-}}{\text{L}} \times \frac{31,000 \text{ mg}}{1 \text{ mol P}} \times \frac{1 \text{ mol P}}{1 \text{ mol } PO_4^{3-}} = 0.23 \text{ ppm P}$$

6. Iron can occur as a carbonate mineral FeCO_3 , which has a $K_{sp} = 3.1 \times 10^{-11}$. Calculate the concentration of iron (ppm) in groundwater in equilibrium FeCO_3 and CaCO_3 . The concentration of $\text{Ca}^{2+}(\text{aq}) = 120$ ppm. Hint: use the K_{sp} of CaCO_3 of 6.0×10^{-9} to estimate the $[\text{CO}_3^{2-}(\text{aq})]$.



↑
common ion
from CaCO_3 dissolution



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

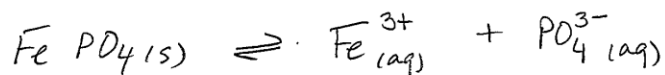
$$= 2.0 \times 10^{-6} \text{ M}$$

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

converting

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

7. Using the solubility of $\text{FePO}_4(\text{s})$ ($K_{\text{sp}} = 1.3 \times 10^{-22}$) and the acidity constants for H_3PO_4 , determine if a concentration of Fe^{3+} of 100. ppm would be sufficient to precipitate 90% of the phosphate from a solution initially containing $1.0 \times 10^{-4} \text{ mol L}^{-1}$ of total phosphate at a constant pH of 8.00.



$$K_{\text{sp}} = [\text{Fe}^{3+}][\text{PO}_4^{3-}] = 1.3 \times 10^{-22}$$

if we add enough iron (III) to maintain a concentration of $\text{Fe}^{3+} = 100. \text{ ppm}$

$$\begin{aligned} \text{then } [\text{Fe}^{3+}] &= 100. \frac{\text{mg}}{\text{L}} \times \frac{1 \text{ mol}}{55.85 \text{ g}} \times \frac{1 \text{ g}}{10^3 \text{ mg}} \\ &= 1.80 \times 10^{-3} \text{ M} \end{aligned}$$

$$\text{and } \therefore [\text{PO}_4^{3-}] = \frac{K_{\text{sp}}}{[\text{Fe}^{3+}]} = \frac{1.3 \times 10^{-22}}{1.8 \times 10^{-3}} = 7.26 \times 10^{-20} \text{ M}$$

$$[\text{PO}_4]_{\text{T}}^{\text{initial}} = 1.0 \times 10^{-4} \text{ M}$$

$$[\text{PO}_4]_{\text{T}}^{\text{equil}} = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]$$

$\nearrow \approx 0$ (at pH 8)

use $K_{\text{a}3}$ & $K_{\text{a}2}$ expressions

$$K_{\text{a}3} = \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} \quad \therefore [\text{HPO}_4^{2-}] = \frac{(10^{-8.0})(7.26 \times 10^{-20})}{(4.2 \times 10^{-13})}$$

$$= 1.73 \times 10^{-15} \text{ M}$$

$$K_{\text{a}2} = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \quad \therefore [\text{H}_2\text{PO}_4^-] = \frac{(10^{-8.0})(1.73 \times 10^{-15})}{(6.3 \times 10^{-8})}$$

$$= 2.74 \times 10^{-16} \text{ M}$$

Therefore, after equilibration with
 $[Fe^{3+}] = 1.8 \times 10^{-3} M$ and $pH = 8.0$,
we have

$$\begin{aligned} [PO_4]_T^{equil.} &= (2.7 \times 10^{-16} + 1.7 \times 10^{-15} + 7.3 \times 10^{-20}) M \\ &= 1.97 \times 10^{-15} M \end{aligned}$$

Since $[PO_4]_T^{initial} = 1.0 \times 10^{-4} M$

if $[PO_4]_T^{equil.} < 1.0 \times 10^{-5} M$

then $> 90\%$ ortho phosphate removed!

YES.

8. Gold ores are frequently leached with cyanide dissolving the gold according to;
 $\text{Au(s)} + 2 \text{CN}^{\text{(aq)}} + \frac{1}{4} \text{O}_2(\text{g}) + \frac{1}{2} \text{H}_2\text{O(l)} \rightleftharpoons \text{Au(CN)}_2^{\text{(aq)}} + \text{OH}^{\text{(aq)}}$
 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 Au(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.

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

\swarrow 10^{-5} M
 \nwarrow 0.032 atm

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

from K_{eq} expression, we can write

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

and rearranging the fractional abundance expression yields,

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

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

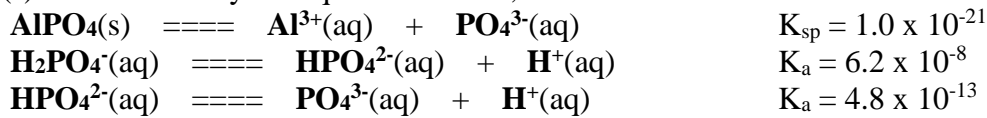
$$\text{and } [\text{Au(CN)}_2^-] = \frac{0.98}{0.02} [\text{CN}^-] = 49 [\text{CN}^-]$$

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

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

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

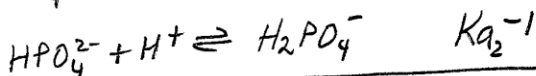
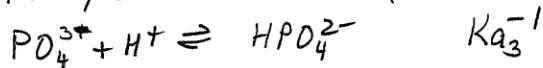
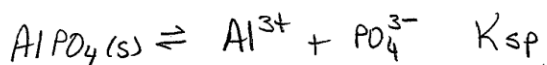
9. Filter alum $\text{Al}_2(\text{SO}_4)_3$ is often used to remove phosphate from wastewater. A wastewater of pH 5.62 containing 25 ppm total phosphate is treated with alum until the equilibrium concentration of Al^{3+} is $4.0 \times 10^{-9} \text{ mol L}^{-1}$. What fraction of the phosphate is precipitated as $\text{AlPO}_4(\text{s})$? Consider only the equilibria below;



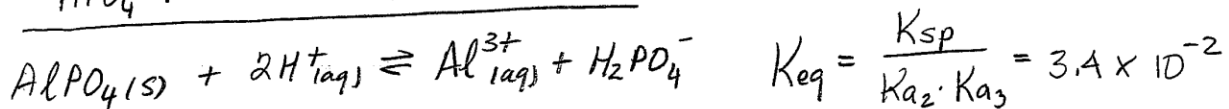
$$\begin{aligned} [\text{PO}_4]_{\text{T}}^{\text{initial}} &= 25 \frac{\text{mg PO}_4}{\text{L}} \times \frac{1 \text{ mol}}{95,000 \text{ mg}} = 2.6 \times 10^{-4} \frac{\text{mol}}{\text{L}} \\ &= [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] \end{aligned}$$

$$[\text{H}^+] = 10^{-5.62} = 2.4 \times 10^{-6} \text{ M}$$

$$\alpha_{\text{PO}_4}^{\text{precipitated}} = \frac{[\text{PO}_4]_{\text{T}}^{\text{initial}} - [\text{PO}_4]_{\text{T}}^{\text{equil.}}}{[\text{PO}_4]_{\text{T}}^{\text{initial}}}$$



at pH = 5.62
 H_2PO_4^- is dominant
form of orthophosphate



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

$$\therefore [\text{H}_2\text{PO}_4^-] = \frac{K_{\text{eq}} \cdot [\text{H}^+]^2}{[\text{Al}^{3+}]} = 4.8 \times 10^{-5} \text{ M}$$

use K_{a_2} to calc. $[\text{HPO}_4^{2-}]$; $K_{\text{a}_2} = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$

$$\therefore [\text{HPO}_4^{2-}] = \frac{K_{\text{a}_2} \cdot [\text{H}_2\text{PO}_4^-]}{[\text{H}^+]} = 1.3 \times 10^{-6} \text{ M}$$

$$\text{So } [\text{PO}_4]_{\text{T}}^{\text{equil.}} \approx [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] = 4.9 \times 10^{-5} \text{ M}$$

$$\therefore \alpha_{\text{PO}_4}^{\text{precipitated}} = \frac{(2.6 \times 10^{-4} - 4.9 \times 10^{-5})}{(2.6 \times 10^{-4})} = 0.81$$

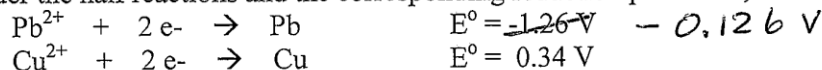
81% ppte ↓

10. 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 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,



0.466 V

Therefore, at standard state (i.e., $[\text{Pb}^{2+}] = [\text{Cu}^{2+}] = 1.0\text{M}$), $E^\circ = 1.60\text{V}$

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.

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

$$E = E^\circ - \frac{2.3RT}{nF} \log Q = \cancel{1.60\text{V}} - \frac{2.3(8.314 \text{ Jmol}^{-1} \text{ K}^{-1})(298 \text{ K})}{2(96485 \text{ Cmol})} \log \frac{4.8 \times 10^{-8}}{1.6 \times 10^{-6}} = \cancel{1.64\text{V}}$$

0.506 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.