

CHEM 301 Assignment #2

Provide solutions to the following questions in a neat and well organized manner.
Reference data sources for any constants and state assumptions, if any.

Due date: Thursday, Oct 18th, 2018

1. Hydrogen sulfide (H_2S) is considerably more toxic to fish than either HS^- or S^{2-} . If hydrogen sulfide concentrations greater than 0.15 mg/L (as S) are harmful to fish health, calculate the minimum safe pH, if the total sulfide concentration is determined to be 20 μM .

Strategy: This question requires a minimum pH in order to maintain the conc. of H_2S below a threshold of 0.15 mg/L S. It will require knowledge of the acid dissociation constants K_{a1} and K_{a2} for H_2S and a unit conversion.

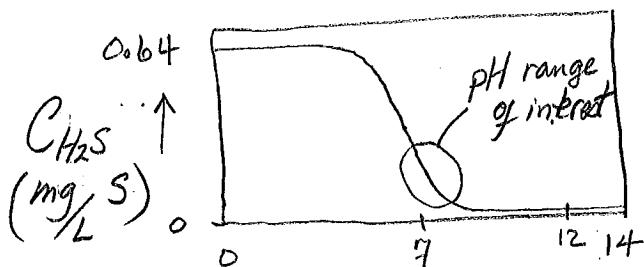
Solution:

converting total sulfide concentration $[\text{H}_2\text{S}]_T$

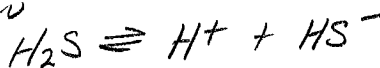
$$20 \times 10^{-6} \frac{\text{mol}}{\text{L}} \times \frac{32,065 \text{ mg}}{\text{mol}} = 0.64 \frac{\text{mg}}{\text{L}} \text{ S}$$

$$K_{a1}(\text{H}_2\text{S}) = 9.0 \times 10^{-8} \quad \therefore \text{p}K_{a1} = 7.05$$

$$K_{a2}(\text{H}_2\text{S}) \approx 1 \times 10^{-12} \quad \therefore \text{p}K_{a2} = 12$$



We can solve this problem considering only 1st dissociation given



$$K_{a1} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}$$

$$\alpha_{\text{H}_2\text{S}} \approx \frac{[\text{H}_2\text{S}]}{[\text{H}_2\text{S}] + [\text{HS}^-]} \quad \text{at pH near } \text{p}K_{a1}$$

$$\therefore \alpha_{\text{H}_2\text{S}} \approx \frac{[\text{H}^+]}{[\text{H}^+] + K_{a1}} \quad \text{and we want } [\text{H}^+] \text{ at which}$$

$$\alpha_{\text{H}_2\text{S}} \leq \frac{0.15}{0.64} = 0.23$$

$$0.23 = \frac{[H^+]}{[H^+] + K_{a1}}$$

$$0.23([H^+] + 9.0 \times 10^{-8}) = [H^+]$$

$$0.23[H^+] + 2.1 \times 10^{-8} = [H^+]$$

$$[H^+](1 - 0.23) = 2.1 \times 10^{-8}$$

$$\therefore [H^+] = \frac{2.1 \times 10^{-8}}{(1 - 0.23)} = 2.7 \times 10^{-8} \text{ M}$$

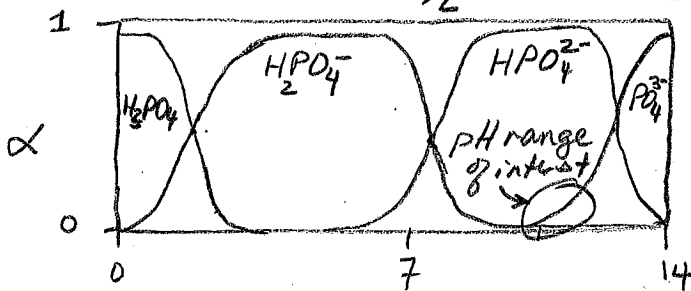
and $\boxed{\text{pH} \approx 7.6}$

2. Phosphoric acid is a triprotic acid (H_3PO_4), $\text{pK}_{a1} = 2.15$, $\text{pK}_{a2} = 7.20$ & $\text{pK}_{a3} = 12.38$. What is the molar concentration of the PO_4^{3-} ion if the total orthophosphate ($[\text{PO}_4^{3-}]_T$) concentration is reported to be 10. mg/L of $\text{PO}_4^{3-}\text{-P}$ at a pH of 9.50.

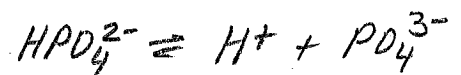
Strategy: Use the definition of the total phosphate in terms of contributing species

$$[\text{PO}_4^{3-}]_T = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] \Rightarrow 10. \frac{\text{mg P}}{\text{L}}$$

$$= 10. \frac{\text{mg}}{\text{L}} \text{ P} \times \frac{1 \text{ mol}}{30,973 \text{ mg}} = 3.23 \times 10^{-4} \text{ M}$$



Solve using K_{a3}



$$\text{and } [\text{H}^+] = 10^{-9.50} \text{ M}$$

Given $\alpha_{\text{H}_3\text{PO}_4}$ & $\alpha_{\text{H}_2\text{PO}_4^-}$ NO at pH = 9.50

Solution: $K_{a3} = \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = 10^{-12.38}$

$$[\text{PO}_4^{3-}] = \frac{K_{a3} \cdot [\text{HPO}_4^{2-}]}{[\text{H}^+]}$$

$$\text{and } [\text{PO}_4^{3-}]_T \approx [\text{HPO}_4^{2-}] = 3.23 \times 10^{-4} \text{ M}$$

$$\therefore [\text{PO}_4^{3-}] = \frac{(10^{-12.38})(3.23 \times 10^{-4})}{(10^{-9.50})} = \frac{1.35 \times 10^{-16}}{3.16 \times 10^{-10}}$$

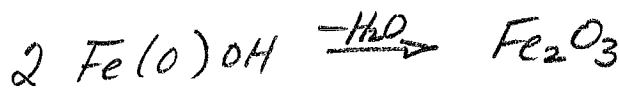
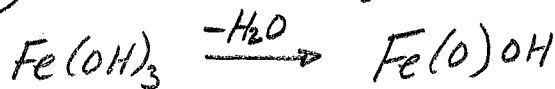
$$= 4.3 \times 10^{-7} \text{ M}$$

An exact solution, using $\alpha_{\text{PO}_4^{3-}}$ in terms of K_{a1} , K_{a2} and K_{a3} yields nearly identical result.

3. A small pond in an area affected by acid mine drainage is observed to have freshly precipitated $\text{Fe}(\text{OH})_3(\text{s})$ at pH 4.
- What is the chemical relationship between $\text{Fe}(\text{OH})_3$, $\text{FeO}(\text{OH})$ and Fe_2O_3 ?
 - An ORP measurement of 190 mV (versus an internal silver/silver chloride reference electrode) was recorded. Is this consistent with the pe of air saturated surface water at this pH in redox equilibrium with the atmosphere?
 - Predict the dominant chemical speciation of carbon, sulfur and nitrogen under these conditions. Justify your answer.
 - What additional information would be useful in choosing the appropriate pe-pH (Pourbaix) diagram for copper, lead and zinc?

Solution

a) They are related by degrees of hydration



metal hydroxides
form first and
dehydrate slowly
over time
to yield
metal oxides

$\text{Fe}(\text{OH})_3$ - iron (III) hydroxide

$\text{Fe}(\text{O})\text{OH}$ - iron (III) hydrous oxide

Fe_2O_3 - iron (III) oxide

b) ORP measured versus Ag/AgCl reference needs to be corrected by the potential of Ag/AgCl vs standard hydrogen electrode.

$$\therefore E_h = \underset{\substack{\uparrow \\ \text{observed}}}{190 \text{ mV}} + \underset{\substack{\uparrow \\ \text{Ag/AgCl}}}{220 \text{ mV}} = 410 \text{ mV (vs SHE)}$$

$$E_h = 0.410 \text{ V} \quad \therefore pe = \frac{0.410 \text{ V}}{0.0591 \text{ V}} = 6.9$$

Using air saturated sample we can also calculate the pe of water assuming redox equilibrium



$$\text{pe} = \text{pe}^\circ - \left(\frac{4}{4}\right)\text{pH} - \left(\frac{1}{4}\right)\log \frac{1}{P_{\text{O}_2}}$$

when $\text{pH} = 4.0$ & $P_{\text{O}_2} = 0.21 \text{ atm}$

$$= 20.8 - (1)4.0 - \frac{1}{4}(\log \frac{1}{0.21})$$

$$= 16.8 - 0.17 = 16.6$$

c) Use pe-pH diagrams at $\text{pH} = 4$ and $\text{pe} \sim 7-17$

carbon $\rightarrow \text{CO}_2(\text{aq}) / \text{H}_2\text{CO}_3(\text{aq})$

sulfur $\rightarrow \text{SO}_4^{2-}(\text{aq})$

nitrogen $\rightarrow \text{NO}_3^-(\text{aq})$

d) We should have some information of total concentration of each metal as well as that of anions that form insoluble precipitates (eg. CO_3^{2-} and S^{2-})

4. A treated wastewater sample has been analyzed to contain the following species.

$$[\text{HCN}]_T = 2.0 \times 10^{-5} \text{ M}$$

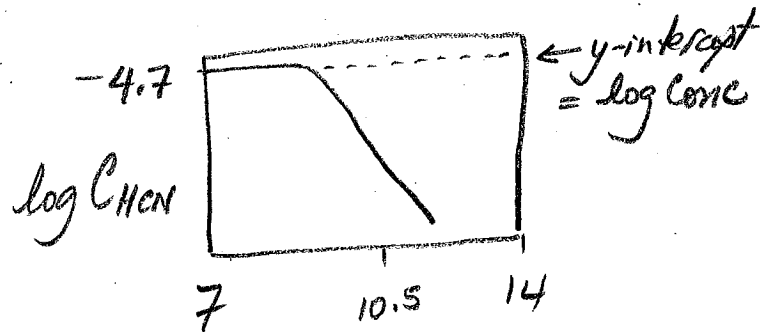
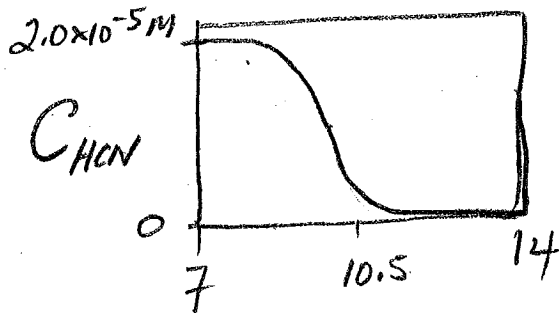
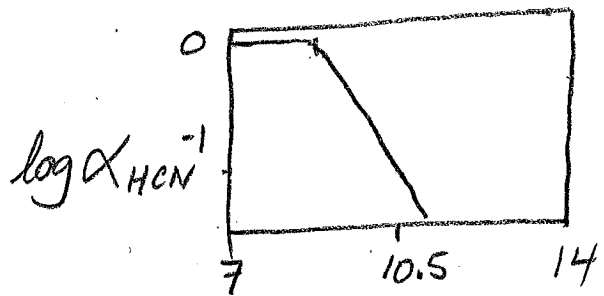
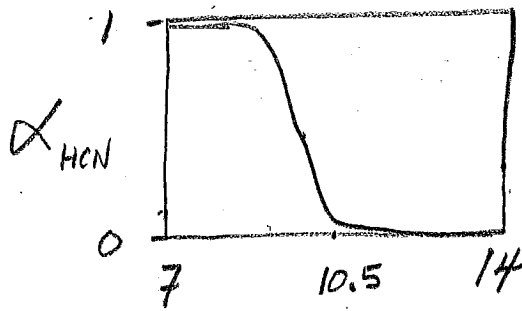
$$[\text{NH}_3]_T = 7.9 \times 10^{-4} \text{ M}$$

Using the corresponding pK_a values, sketch a plot of $\log \text{Conc (M)}$ vs pH for the relevant chemical speciation (protonation states) between $\text{pH } 4$ and 10 . Compare this with an overlay plot constructed using Excel.

strategy: Use K_a values to identify pH where acidic & basic forms are in equal abundance (ie. $\text{pH} = \text{p}K_a$ when $[\text{HA}] = [\text{A}^-]$)

$$K_a(\text{HCN}) = 6.2 \times 10^{-10}, \text{p}K_a(\text{HCN}) = 9.21$$

$$K_a(\text{NH}_4^+) = 5.6 \times 10^{-10}, \text{p}K_a(\text{NH}_4^+) = 9.25$$

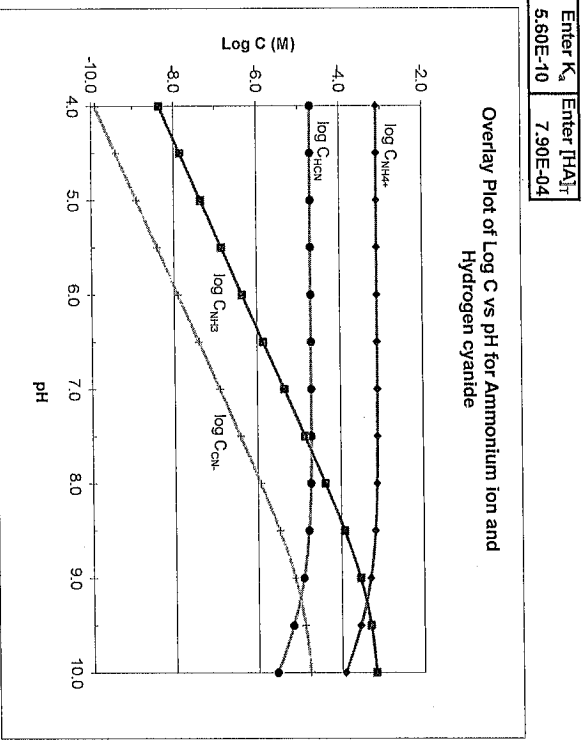


α and Conc plots are sigmoidal curves

↑
log plots have slope = 0 or ± 1

pH Speciation for ammonium and hydrogen cyanide

pH	[H ⁺]	$K_{NH_4^+}$	K_{HCN}	$\log C_{NH_4^+}$	$\log C_{NH_3}$	$\log C_{CNH_2}$	$\log C_{CN^-}$	$\log C_{C_{tot}}$
0.0	1.00	1.00E+00	5.60E-10	-2.43E-10	-9.25	-3.10	-12.35	5.60E-10
0.5	0.32	1.00E+00	1.77E-09	-7.69E-10	-8.75	-3.10	-11.85	6.20E-10
1.0	0.10	1.00E+00	5.60E-09	-2.43E-09	-8.25	-3.10	-11.35	6.20E-10
1.5	0.03	1.00E+00	1.77E-08	-7.69E-08	-7.75	-3.10	-10.85	6.20E-10
2.0	0.01	1.00E+00	5.60E-08	-2.43E-08	-7.25	-3.10	-10.35	6.20E-10
2.5	0.00	1.00E+00	1.77E-07	-7.69E-07	-6.75	-3.10	-9.85	6.20E-10
3.0	0.00	1.00E+00	5.60E-07	-2.43E-07	-6.25	-3.10	-9.35	6.20E-10
3.5	0.00	1.00E+00	1.77E-06	-7.69E-06	-5.75	-3.10	-8.85	6.20E-10
4.0	0.00	1.00E+00	5.60E-06	-2.43E-06	-5.25	-3.10	-8.35	6.20E-10
4.5	0.00	1.00E+00	1.77E-05	-7.69E-05	-4.75	-3.10	-7.85	6.20E-10
5.0	0.00	1.00E+00	5.60E-05	-2.43E-05	-4.25	-3.10	-7.35	6.20E-10
5.5	0.00	1.00E+00	1.77E-04	-7.69E-04	-3.75	-3.10	-6.85	6.20E-10
6.0	0.00	9.99E-01	5.60E-04	-2.43E-04	-3.25	-3.10	-6.35	6.20E-10
6.5	0.00	9.98E-01	1.77E-03	-7.68E-03	-2.75	-3.10	-5.85	6.20E-10
7.0	0.00	9.94E-01	5.57E-03	-2.43E-03	-2.25	-3.10	-5.36	6.20E-10
7.5	0.00	9.83E-01	1.74E-02	-7.67E-02	-1.76	-3.11	-4.86	6.20E-10
8.0	0.00	9.47E-01	5.30E-02	-2.37E-02	-1.28	-3.13	-4.38	6.20E-10
8.5	0.00	8.50E-01	1.50E-01	-7.08E-02	-0.82	-3.17	-3.92	6.20E-10
9.0	0.00	6.41E-01	3.59E-01	-1.93E-01	-0.44	-3.30	-3.55	6.20E-10
9.5	0.00	3.61E-01	6.39E-01	-4.49E-01	-0.19	-3.54	-3.30	6.20E-10
10.0	0.00	1.52E-01	8.48E-01	-8.20E-01	-0.07	-3.92	-3.17	6.20E-10
10.5	0.00	5.35E-02	9.47E-01	-1.27E+00	-0.02	-4.37	-3.13	6.20E-10
11.0	0.00	1.75E-02	9.82E-01	-1.76E+00	-0.01	-4.86	-3.11	6.20E-10
11.5	0.00	5.62E-03	9.94E-01	-2.25E+00	0.00	-5.35	-3.10	6.20E-10
12.0	0.00	1.78E-03	9.98E-01	-2.75E+00	0.00	-5.85	-3.10	6.20E-10
12.5	0.00	5.64E-04	9.99E-01	-3.25E+00	0.00	-6.35	-3.10	6.20E-10
13.0	0.00	1.79E-04	1.00E+00	-4.25E+00	0.00	-6.85	-3.10	6.20E-10
13.5	0.00	5.65E-05	1.00E+00	-4.75E+00	0.00	-7.35	-3.10	6.20E-10
14.0	0.00	1.79E-05	1.00E+00	-4.79E+00	0.00	-7.85	-3.10	6.20E-10



Enter K_a 6.20E-10 Enter [H⁺] 2.00E-05

5. A speciation diagram for thallium (III) as a function of pH and chloride concentration is attached. Estimate the value of the formation constants ($\beta_1 - \beta_4$) and the acidity constants ($K_{a1} - K_{a4}$). Justify your answers.

Strategy: identify regions on speciation diagram that correspond to the chemical equilibrium of interest. use the boundary to estimate either the pH or $\log [Cl^-]$ at which two Tl(III) species are present at same concentration.

Solution:

K_{a1} for Tl^{3+} defined by $Tl^{3+} + H_2O \rightleftharpoons Tl(OH)^{2+} + H^+$

$$\therefore K_{a1} = \frac{[Tl(OH)^{2+}][H^+]}{[Tl^{3+}]} \text{ and at boundary}$$

$$[Tl^{3+}] = [Tl(OH)^{2+}] \therefore K_{a1} = [H^+]$$

and $pK_{a1} = pH$ @ boundary

Reading pH at boundaries $Tl^{3+}/Tl(OH)^{2+}$, $pH = 2.7$

$Tl(OH)^{2+}/Tl(OH)_2^+$, $pH = 6.3$

$Tl(OH)_2^+/Tl(OH)_3$, $pH = 7.4$

$Tl(OH)_3/Tl(OH)_4^-$, $pH = 8.8$

$$\therefore K_{a1} \cong 10^{-2.7} = 2.0 \times 10^{-3}$$

$$K_{a2} \cong 10^{-6.3} = 5.0 \times 10^{-7}$$

$$K_{a3} \cong 10^{-7.4} = 4.0 \times 10^{-8}$$

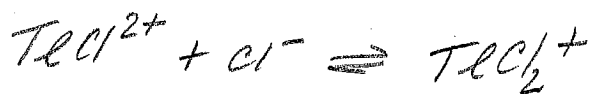
$$K_{a4} \cong 10^{-8.8} = 1.6 \times 10^{-9}$$

Similarly for the boundaries between thallium chloride species.

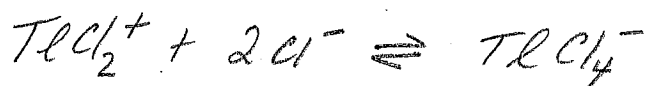


$$K_{f1} = \frac{[\text{TlCl}^{2+}]}{[\text{Tl}^{3+}][\text{Cl}^-]} \quad \text{and at boundary} \quad [\text{Tl}^{3+}] = [\text{TlCl}^{2+}]$$

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



$$K_{f2} = \frac{1}{[\text{Cl}^-]}, \text{ when } [\text{TlCl}^{2+}] = [\text{TlCl}_2^+]$$



$$K_{f3} \cdot K_{f4} = \frac{1}{[\text{Cl}^-]^2}$$

Reading $\log[\text{Cl}^-]$ from plot:

$$K_{f1} = \frac{1}{10^{-8.1}} = 1.3 \times 10^8$$

$$K_{f2} = \frac{1}{10^{-5.4}} = 2.5 \times 10^5$$

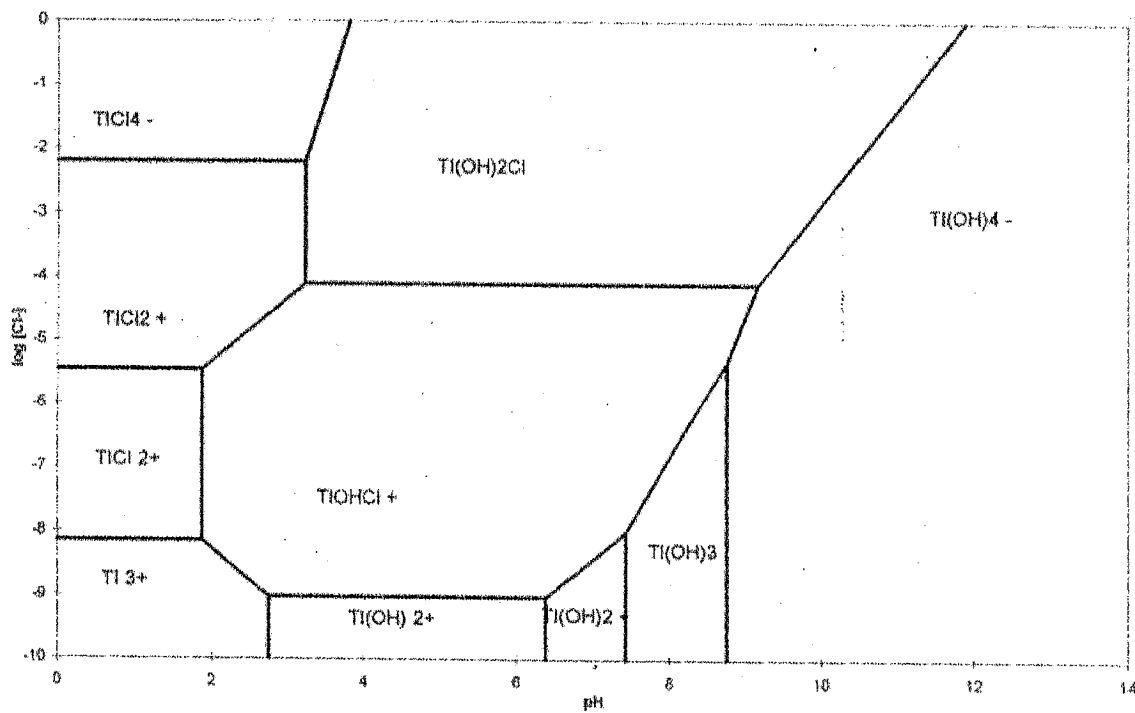
$$K_{f3} \cdot K_{f4} = \frac{1}{10^{-2.2}} = 1.6 \times 10^2$$

$$\beta_1 = K_{f1} = 1.3 \times 10^8$$

$$\beta_2 = K_{f1} \cdot K_{f2} = 3.3 \times 10^{13}$$

$$\beta_4 = K_{f1} \cdot K_{f2} \cdot K_{f3} \cdot K_{f4} = 5.2 \times 10^{15}$$

$$\text{when } [\text{TlCl}_2^+] = [\text{TlCl}_4^-]$$

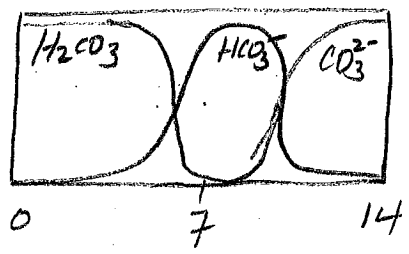


Chemical speciation diagram for Thallium (III) species as a function of pH and pChloride.

6. Determine the concentration of cadmium ion in equilibrium with cadmium carbonate in a water sample buffered at a pH of 8.10 with a total alkalinity of 32 mg/L as CaCO_3 . The $\text{p}K_{\text{sp}}$ of CdCO_3 is 13.74.

Strategy: When $\text{CdCO}_3(\text{s})$ dissolves in water at $\text{pH} = 8.10$, it will produce $\text{Cd}^{2+}(\text{aq})$ and $\text{HCO}_3^-(\text{aq})$.

recall pH speciation diagram for H_2CO_3



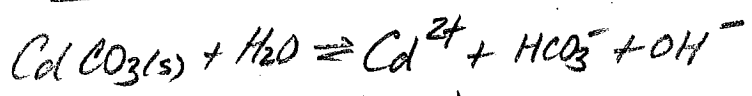
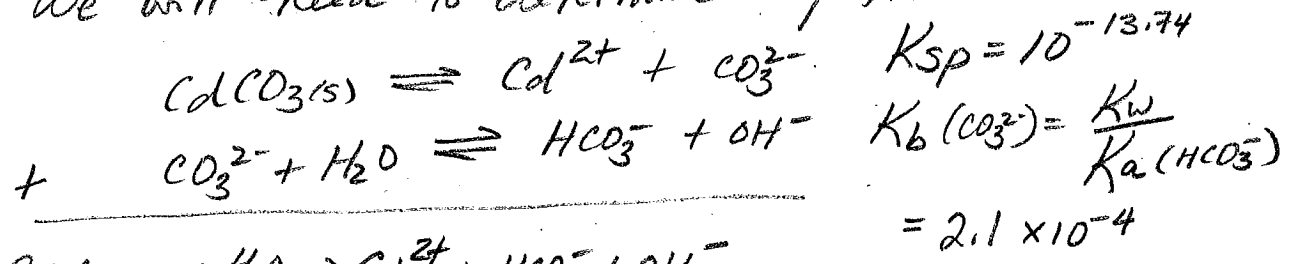
Solution: $K_{\text{eq}} = [\text{Cd}^{2+}][\text{HCO}_3^-][\text{OH}^-]$

$$\therefore [\text{Cd}^{2+}] = \frac{K_{\text{eq}}}{[\text{HCO}_3^-][\text{OH}^-]}$$

where $[\text{HCO}_3^-] \approx [\text{alk}]_T$ @ $\text{pH} 8.10$

and $[\text{OH}^-] = 10^{-(14.00 - 8.10)}$ at 25°C

We will need to determine K_{eq} from other rxn's



$$K_{\text{eq}} = \frac{K_{\text{sp}} \cdot K_{\text{w}}}{K_{\text{a}}(\text{HCO}_3^-)} = 3.8 \times 10^{-18}$$

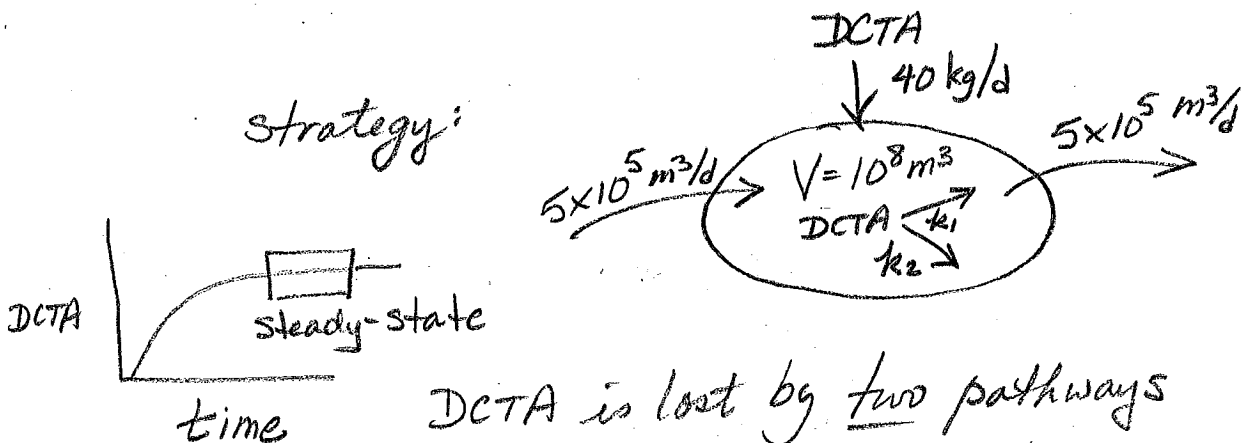
$$[\text{alk}]_T = 32 \frac{\text{mg CaCO}_3}{\text{L}} \times \frac{1 \text{ mol}}{100.08 \text{ g}} \times \frac{1 \text{ g}}{10^3 \text{ mg}} \times \frac{2 \text{ mol H}^+}{1 \text{ mol CaCO}_3}$$
$$= 6.40 \times 10^{-4} \frac{\text{mol}}{\text{L}}$$

$$[\text{OH}^-] = 10^{-(14.00 - 8.10)} = 10^{-5.90}$$
$$= 1.26 \times 10^{-6} \frac{\text{mol}}{\text{L}}$$

$$\therefore [\text{Cd}^{2+}] = \frac{3.8 \times 10^{-18}}{(6.40 \times 10^{-4})(1.26 \times 10^{-6})}$$
$$= 4.72 \times 10^{-9} \text{ M}$$

$$\text{or } 0.53 \frac{\mu\text{g}}{\text{L}} \text{ Cd}$$

7. Lake Phillip is well mixed and has a volume of 10^8 m^3 . A single river flowing at $5 \times 10^5 \text{ m}^3 \text{ day}^{-1}$ feeds it. Water exits Lake Phillip via the Andrew River and evaporation is negligible. For several years, a local industry has been dumping 40 kg day^{-1} of a pollutant DCTA into the lake. DCTA disappears from the lake via two processes: it flows out of the lake in the Andrew River and it chemically degrades with a half-life of 48 days. What is the steady state concentration of DCTA in Lake Phillip?



DCTA is lost by two pathways
 one of these is related to water residence time
 the other is a degradation pathway.

Solution:

$$\tau_w = \frac{10^8 \text{ m}^3}{5 \times 10^5 \text{ m}^3/\text{d}} = 200 \text{ days}$$

$$\tau_p \neq \tau_w$$

$$\tau_p = \frac{1}{\sum k_1 + k_2}$$

if k_1 is related to flushing, then $\tau_w = \frac{1}{k_1}$
 and k_2 is related to degradation, then $t_{1/2} = \frac{0.693}{k_2}$

$$\therefore k_1 = 5.0 \times 10^{-3} \text{ d}^{-1} \text{ and } k_2 = 1.4 \times 10^{-2} \text{ d}^{-1}$$

$$\text{and } \tau_p = \frac{1}{1.9 \times 10^{-2} \text{ d}^{-1}} = 51 \text{ d} = \frac{\text{stock}}{\text{flux}}$$

$$\therefore \text{stock} = (51 \text{ d})(40 \text{ kg/d}) = 2060 \text{ kg}$$

$$\rightarrow [\text{DCTA}] = \frac{2060 \text{ kg}}{10^8 \text{ m}^3 \cdot \frac{10^3 \text{ kg}}{\text{m}^3}}$$

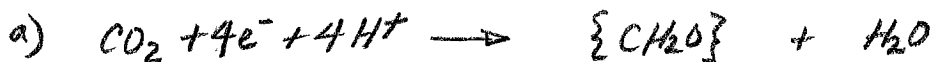
8. For each of the following, derive an equation of the line for the redox boundary in the form of $pe = m \text{ pH} + b$ (See further Appendix B.4 and B.5 of the textbook).

a) CO_2 and $\{\text{CH}_2\text{O}\}$

b) SO_4^{2-} and H_2S

c) HOCl and Cl^-

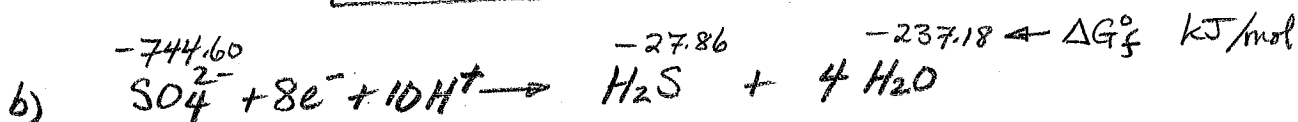
d) $\text{MnO}_2(\text{s})$ and Mn^{2+} in a solution containing manganese (II) ion at an activity of 10^{-5}



$$pe = pe^\circ - \frac{4}{4} \text{pH} - \frac{1}{4} \log \frac{\{\text{CH}_2\text{O}\}}{\{\text{CO}_2\}}$$

$$pe^\circ = -1.20$$

$$\therefore \boxed{pe = -1.20 - \text{pH}}$$

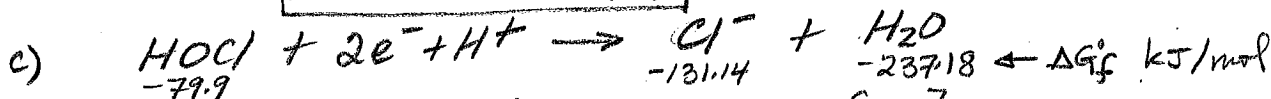


$$pe = pe^\circ - \frac{10}{8} \text{pH} - \frac{1}{8} \log \frac{\{\text{H}_2\text{O}\}}{\{\text{SO}_4^{2-}\}}$$

$$\Delta G^\circ = -231.98 \text{ kJ/mol}$$

$$pe^\circ = \frac{1 \Delta G^\circ}{n e 2.3 RT} = \frac{-231,980 \text{ J mol}^{-1}}{8(2.3)(8.314 \text{ J mol}^{-1} \text{K}^{-1})(298 \text{ K})} = 5.08$$

$$\therefore \boxed{pe = 5.08 - 1.25 \text{pH}}$$

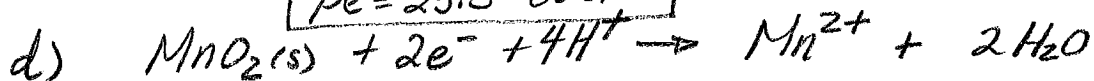


$$pe = pe^\circ - \frac{1}{2} \text{pH} - \frac{1}{2} \log \frac{\{\text{Cl}^-\}}{\{\text{HOCl}\}}$$

$$\Delta G^\circ = -288.4 \text{ kJ/mol}$$

$$pe^\circ = \frac{\Delta G^\circ}{n e 2.3 RT} = \frac{-288,400 \text{ J mol}^{-1}}{(2)(2.3)(8.314 \text{ J mol}^{-1} \text{K}^{-1})(298 \text{ K})} = 25.3$$

$$\boxed{pe = 25.3 - 0.5 \text{pH}}$$



$$pe = pe^\circ - \frac{4}{2} \text{pH} - \frac{1}{2} \log \frac{\{\text{Mn}^{2+}\}}{1}$$

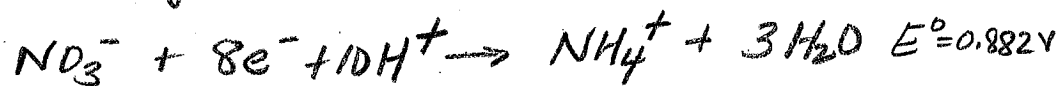
$$pe^\circ = 20.8$$

$$\therefore pe = 20.8 - 2 \text{pH} - \frac{1}{2} \log(10^{-5})$$

$$\boxed{= 23.3 - 2 \text{pH}}$$

9. A water sample with a pH 6.0 was analyzed and found to contain 0.5 mmol/L nitrate ion and 5 $\mu\text{mol/L}$ of ammonium ion. Calculate the pe of this water and predict the ratio of $[\text{Cr}_2\text{O}_7^{2-}]$ to $[\text{Cr}^{3+}]$ in the same sample.

Strategy: Use the $\text{NO}_3^-/\text{NH}_4^+$ conc to predict pe using



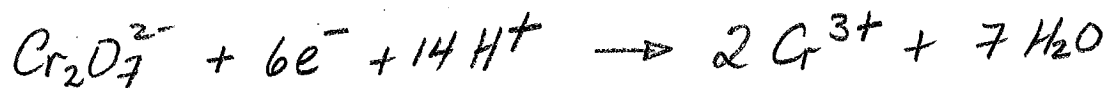
and then use this pe to predict ratio of $\text{Cr}_2\text{O}_7^{2-}$ to Cr^{3+}

Solution:

$$pe = pe^\circ - \frac{10}{8} pH - \frac{1}{8} \log \frac{\{\text{NH}_4^+\}}{\{\text{NO}_3^-\}}$$

$$\text{at } pH = 6.0 \text{ and } [\text{NH}_4^+]/[\text{NO}_3^-] = \frac{5 \times 10^{-6}}{0.5 \times 10^{-3}}$$

$$\begin{aligned} \therefore pe &= pe^\circ - \frac{5}{4}(6.0) - \left(\frac{1}{8}\right)(-2) \\ &= pe^\circ - 7.25 = 14.9 - 7.25 = 7.65 \end{aligned}$$



$$pe = pe^\circ - \left(\frac{14}{6}\right) pH - \left(\frac{1}{6}\right) \log \frac{\{\text{Cr}^{3+}\}^2}{\{\text{Cr}_2\text{O}_7^{2-}\}}$$

$$pe^\circ = 23.0$$

$$pe = 7.65$$

$$pH = 6.0$$

$$7.65 = 23.0 - 14.0 - 0.167 \log \frac{\{\text{Cr}^{3+}\}^2}{\{\text{Cr}_2\text{O}_7^{2-}\}}$$

$$-1.35 = -0.167 \log \frac{\{Cr^{3+}\}^2}{\{Cr_2O_7^{2-}\}}$$

$$8.10 = \log \frac{\{Cr^{3+}\}^2}{\{Cr_2O_7^{2-}\}}$$

$$\therefore \frac{\{Cr^{3+}\}^2}{\{Cr_2O_7^{2-}\}} = 10^{8.10} = 1.26 \times 10^8$$

If the total amt of Cr is known, then we could use $[Cr]_T = [Cr^{3+}] + 2[Cr_2O_7^{2-}]$

$$\text{and } [Cr_2O_7^{2-}] = \frac{[Cr]_T - [Cr^{3+}]}{2}$$

which we could substitute in above to solve for $[Cr^{3+}] / [Cr_2O_7^{2-}]$ exactly using the quadratic formula.

$$\frac{[Cr^{3+}]^2}{\frac{1}{2}[Cr]_T - \frac{1}{2}[Cr^{3+}]} = 1.26 \times 10^8$$

$$[Cr^{3+}]^2 = 6.30 \times 10^7 [Cr]_T - 6.30 \times 10^7 [Cr^{3+}]$$

$$\therefore [Cr^{3+}]^2 + 6.30 \times 10^7 [Cr^{3+}] - 6.30 \times 10^7 [Cr]_T = 0$$

$$\text{let } x = [Cr^{3+}]$$

$$ax^2 + bx + c = 0$$

$$a = 1$$

$$b = 6.30 \times 10^7$$

$$c = -6.30 \times 10^7 ([Cr]_T)$$