CHEM 301 - Assignment #2
SOLUTIONS

1. Hypochlorous acid (HOCl) is a considerably more effective dis-infectant than it's conjugate base (OCl). What concentration (as mg/L Cl_2) needs to be added to a water sample naturally buffered at pH 7.8, in order to achieve a HOCl concentration of 1.0 mg/L (as Cl_2)? pK$_a$ (HOCl) = 7.25

Solution: The relevant chemical equilibria is for the weak acid hypochlorous acid;

$$HOCl \;====\; H^+ + OCl^- \qquad K_a = 10^{-7.25}$$

At a pH near to or above the pK$_a$ (HOCl) it is clear that some HOCl will be converted into OCl^-. One way to approach this problem is to use the fractional abundance expression and determine how much HOCl will need to be added in order to achieve a final concentration of HOCl = 1.0 mg/L as Cl_2.

$$\alpha_{HOCl} = \frac{[HOCl]}{[HOCl]+[OCl^-]}$$

Rearranging the K_a expression and substituting into the fractional abundance expression gives;

$$\alpha_{HOCl} = \frac{[H^+]}{[H^+]+K_a} = \frac{10^{-7.8}}{10^{-7.8}+10^{-7.25}} = 0.221$$

Since we can express [HOCl] = $[HOCl]_T$ x α_{HOCl}, we can rearrange as;

$$[HOCl]_T = \frac{[HOCl]}{\alpha_{HOCl}} = \frac{1.0\,mg/LCl_2}{0.221} = 4.5\,mg/LCl_2$$

Thus, if we add 4.5 mg/L as Cl_2 and 22.1 % of this remains as HOCl, then we are left with a resulting concentration of 1.0 mg/L as Cl_2 as required.

2. Plot a fully labeled pH speciation diagram for the silicic acid system H_4SiO_4-$H_3SiO_4^-$-$H_2SiO_4^{2-}$ system over the pH range of 0 to 14. $K_{a1} = 2.2 \times 10^{-10}$, $K_{a2} = 6.3 \times 10^{-14}$. Use a spreadsheet program (such as Excel) for repetitive calculations and to plot curves for fractional abundance as a function of pH (0 – 14) for each species. What form of silicic acid predominates in natural waters?

Solution: The pKa's for the first and second deprotonation of silicic acid are pK$_{a1}$ = 9.66 and pK$_{a2}$ = 13.2, which suggest that there will be three chemical forms present over the pH range 0 – 14.

H_4SiO_4 will dominante below pH 9.7
$H_3SiO_4^-$ will dominante between pH 9.7 and 13.2
and
$H_2SiO_4^{2-}$ will dominante above pH 13.2

Writing the expressions for the fractional abundance and making appropriate substitutions from the K_{a1} and K_{a2} expressions yields;

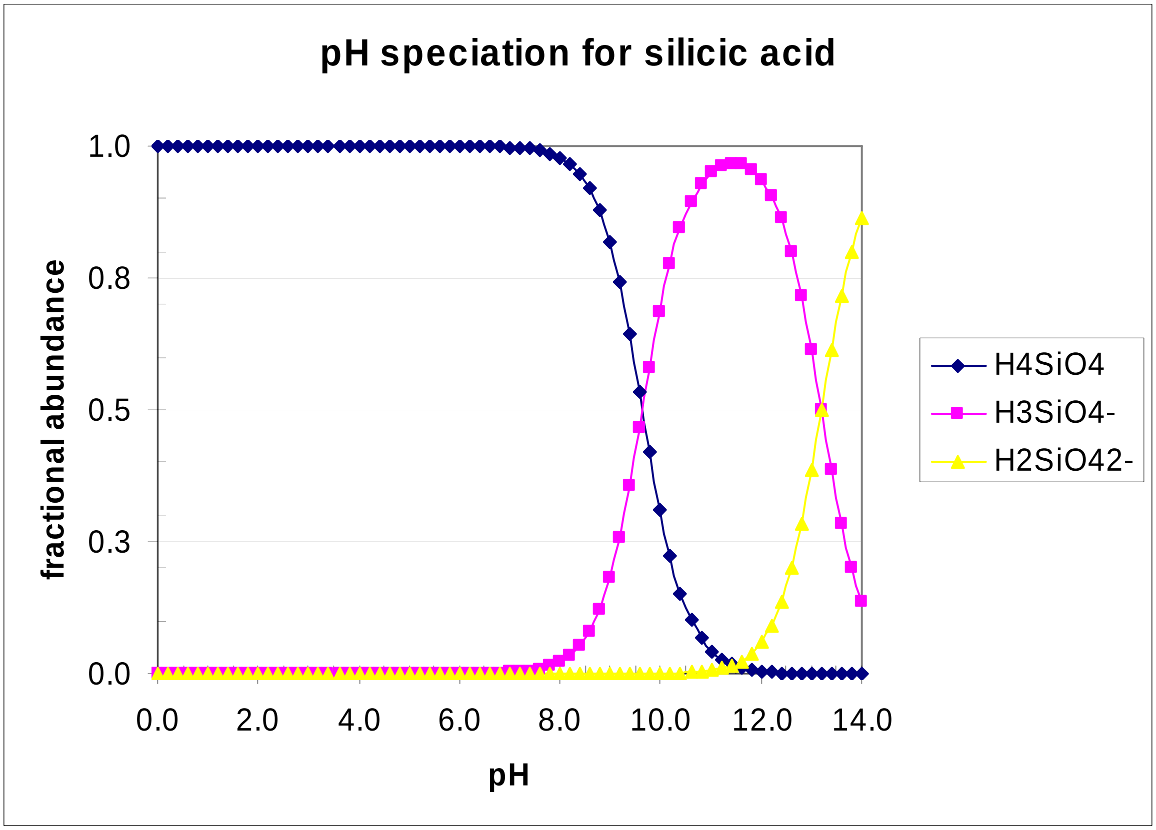
$$\alpha_{\mathrm{H4SiO4}} = \frac{[\mathrm{H_4SiO_4}]}{[\mathrm{H_4SiO_4}]_\mathrm{T}} = \frac{[H^+]^2}{[H+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

Similarly for the fractional abundance for the conjugate bases;

$$\alpha_{\mathrm{H3SiO4-}} = \frac{[\mathrm{H_3SiO_4^-}]}{[\mathrm{H_4SiO_4}]_\mathrm{T}} = \frac{\mathrm{K_{a1}}[H^+]}{[H+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

$$\alpha_{\mathrm{H2SiO42-}} = \frac{[\mathrm{H2SiO_4^{2-}}]}{[\mathrm{H_4SiO_4}]_\mathrm{T}} = \frac{\mathrm{K_{a1}K_{a2}}}{[H+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

Using Excel to plot the fractional abundance versus pH yields;



It can be seen therefore that over the typical pH of natural waters of 5 -9, the dominant for silicic acid are H_4SiO_4 and $H_3SiO_4^-$.

3. A water sample contains reduced inorganic nitrogen and sulfur with the following reported concentrations. Using Excel, construct an overlay plot of log Conc (M) vs pH for the four species present between pH 4 and 10.

$[S(-II)]_T = 20\ \mu M$
$[N(-III)]_T = 180\ \mu M$

Solution: The reduced sulfur is present as one or more of the following sulfide species

$H_2S/HS^-/S^{2-}$ $pK_{a1} = 7.00$, $pK_{a2} = 11.96$
So, $[S(-II)]_T = [H_2S] + [HS^-] + [S^{2-}] = 20\ \mu M$

And the reduced nitrogen is present as one or more of the following ammonium species;

NH_4^+/NH_3 $pK_a = 9.25$
So, $[N(-III)]_T = [NH_4^+] + [NH_3] = 180\ \mu M$

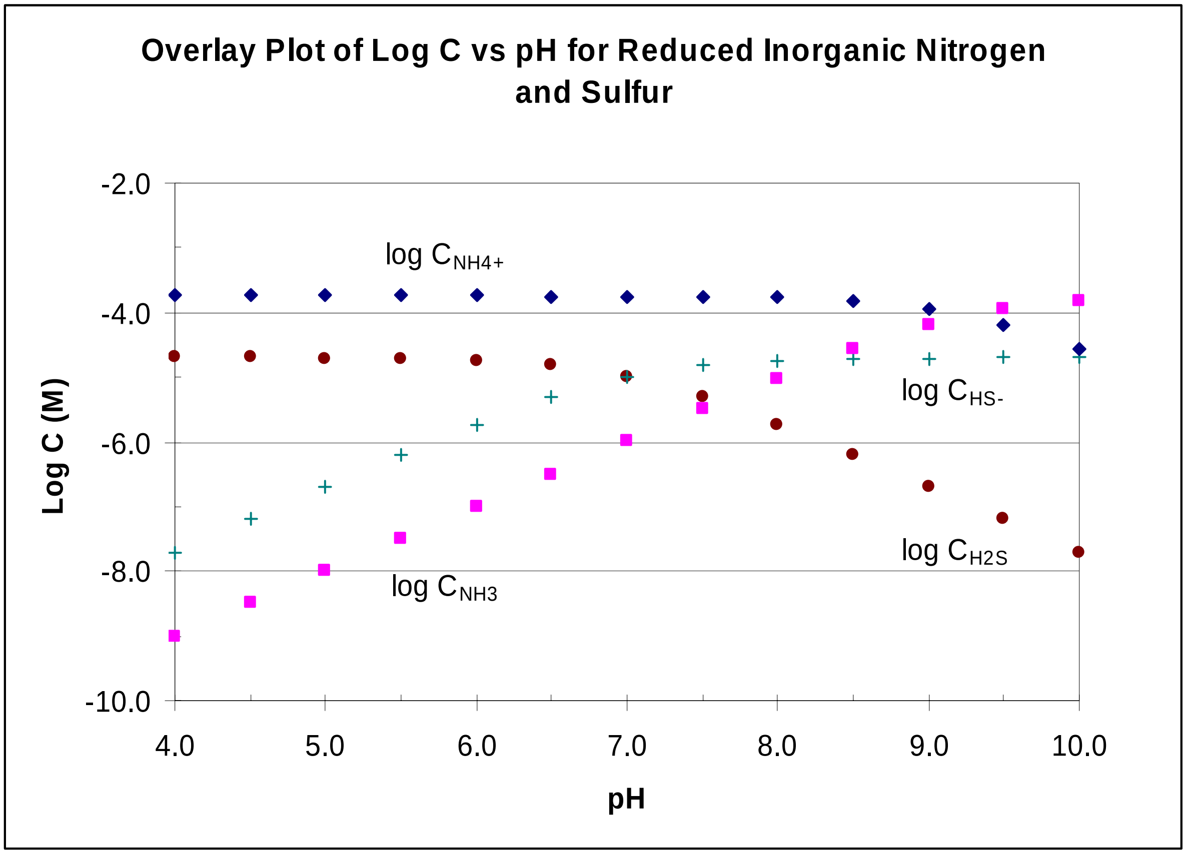
Using the expressions for the fractional abundance as a function of pH, we can use Excel to calculate log Conc of all species over a range of pH's.

$$\alpha_{H2S} = \frac{[H^+]^2}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

and

$$[H_2S] = \alpha_{H2S} \text{ x } [S(-II)]_T$$

Similarly for over species present between pH 4 and 10 (see attached for Spreadsheet).



pH Speciation for ammonium, $[N(-III)]_T = 180\ \mu M$

pH	[H+]	α_{NH4+}	α_{NH3}	log α_{NH4+}	log α_{NH3}	log C_{NH4+}	log C_{NH3}
0.0	1.00	1.00E+00	5.60E-10	-2.43E-10	-9.25	-3.74	-13.00
0.5	0.32	1.00E+00	1.77E-09	-7.69E-10	-8.75	-3.74	-12.50
1.0	0.10	1.00E+00	5.60E-09	-2.43E-09	-8.25	-3.74	-12.00
1.5	0.03	1.00E+00	1.77E-08	-7.69E-09	-7.75	-3.74	-11.50
2.0	0.01	1.00E+00	5.60E-08	-2.43E-08	-7.25	-3.74	-11.00
2.5	0.00	1.00E+00	1.77E-07	-7.69E-08	-6.75	-3.74	-10.50
3.0	0.00	1.00E+00	5.60E-07	-2.43E-07	-6.25	-3.74	-10.00
3.5	0.00	1.00E+00	1.77E-06	-7.69E-07	-5.75	-3.74	-9.50
4.0	0.00	1.00E+00	5.60E-06	-2.43E-06	-5.25	-3.74	-9.00
4.5	0.00	1.00E+00	1.77E-05	-7.69E-06	-4.75	-3.74	-8.50
5.0	0.00	1.00E+00	5.60E-05	-2.43E-05	-4.25	-3.74	-8.00
5.5	0.00	1.00E+00	1.77E-04	-7.69E-05	-3.75	-3.74	-7.50
6.0	0.00	9.99E-01	5.60E-04	-2.43E-04	-3.25	-3.74	-7.00
6.5	0.00	9.98E-01	1.77E-03	-7.68E-04	-2.75	-3.75	-6.50
7.0	0.00	9.94E-01	5.57E-03	-2.43E-03	-2.25	-3.75	-6.00
7.5	0.00	9.83E-01	1.74E-02	-7.62E-03	-1.76	-3.75	-5.50
8.0	0.00	9.47E-01	5.30E-02	-2.37E-02	-1.28	-3.77	-5.02
8.5	0.00	8.50E-01	1.50E-01	-7.08E-02	-0.82	-3.82	-4.57
9.0	0.00	6.41E-01	3.59E-01	-1.93E-01	-0.44	-3.94	-4.19
9.5	0.00	3.61E-01	6.39E-01	-4.43E-01	-0.19	-4.19	-3.94
10.0	0.00	1.52E-01	8.48E-01	-8.20E-01	-0.07	-4.56	-3.82
10.5	0.00	5.35E-02	9.47E-01	-1.27E+00	-0.02	-5.02	-3.77
11.0	0.00	1.75E-02	9.82E-01	-1.76E+00	-0.01	-5.50	-3.75
11.5	0.00	5.62E-03	9.94E-01	-2.25E+00	0.00	-6.00	-3.75
12.0	0.00	1.78E-03	9.98E-01	-2.75E+00	0.00	-6.49	-3.75
12.5	0.00	5.64E-04	9.99E-01	-3.25E+00	0.00	-6.99	-3.74
13.0	0.00	1.79E-04	1.00E+00	-3.75E+00	0.00	-7.49	-3.74
13.5	0.00	5.65E-05	1.00E+00	-4.25E+00	0.00	-7.99	-3.74
14.0	0.00	1.79E-05	1.00E+00	-4.75E+00	0.00	-8.49	-3.74

Enter K_a	Enter $[HA]_T$
5.60E-10	**1.80E-04**

pH Speciation for hydrogen sulfide, $[S(-II)]_T = 20\ \mu M$

pH	[H+]	α_{H2S}	α_{HS-}	log α_{H2S}	log α_{HS-}	log C_{H2S}	log C_{HS-}
0.0	1.00	1.00E+00	1.00E-07	-4.34E-08	-7.00	-4.70	-11.70
0.5	0.32	1.00E+00	3.16E-07	-1.37E-07	-6.50	-4.70	-11.20
1.0	0.10	1.00E+00	1.00E-06	-4.34E-07	-6.00	-4.70	-10.70
1.5	0.03	1.00E+00	3.16E-06	-1.37E-06	-5.50	-4.70	-10.20
2.0	0.01	1.00E+00	1.00E-05	-4.34E-06	-5.00	-4.70	-9.70
2.5	0.00	1.00E+00	3.16E-05	-1.37E-05	-4.50	-4.70	-9.20
3.0	0.00	1.00E+00	1.00E-04	-4.34E-05	-4.00	-4.70	-8.70
3.5	0.00	1.00E+00	3.16E-04	-1.37E-04	-3.50	-4.70	-8.20
4.0	0.00	9.99E-01	9.99E-04	-4.34E-04	-3.00	-4.70	-7.70
4.5	0.00	9.97E-01	3.15E-03	-1.37E-03	-2.50	-4.70	-7.20
5.0	0.00	9.90E-01	9.90E-03	-4.32E-03	-2.00	-4.70	-6.70
5.5	0.00	9.69E-01	3.07E-02	-1.35E-02	-1.51	-4.71	-6.21
6.0	0.00	9.09E-01	9.09E-02	-4.14E-02	-1.04	-4.74	-5.74
6.5	0.00	7.60E-01	2.40E-01	-1.19E-01	-0.62	-4.82	-5.32
7.0	0.00	5.00E-01	5.00E-01	-3.01E-01	-0.30	-5.00	-5.00
7.5	0.00	2.40E-01	7.60E-01	-6.19E-01	-0.12	-5.32	-4.82
8.0	0.00	9.09E-02	9.09E-01	-1.04E+00	-0.04	-5.74	-4.74
8.5	0.00	3.07E-02	9.69E-01	-1.51E+00	-0.01	-6.21	-4.71
9.0	0.00	9.90E-03	9.90E-01	-2.00E+00	0.00	-6.70	-4.70
9.5	0.00	3.15E-03	9.97E-01	-2.50E+00	0.00	-7.20	-4.70
10.0	0.00	9.99E-04	9.99E-01	-3.00E+00	0.00	-7.70	-4.70
10.5	0.00	3.16E-04	1.00E+00	-3.50E+00	0.00	-8.20	-4.70
11.0	0.00	1.00E-04	1.00E+00	-4.00E+00	0.00	-8.70	-4.70
11.5	0.00	3.16E-05	1.00E+00	-4.50E+00	0.00	-9.20	-4.70
12.0	0.00	1.00E-05	1.00E+00	-5.00E+00	0.00	-9.70	-4.70
12.5	0.00	3.16E-06	1.00E+00	-5.50E+00	0.00	-10.20	-4.70
13.0	0.00	1.00E-06	1.00E+00	-6.00E+00	0.00	-10.70	-4.70
13.5	0.00	3.16E-07	1.00E+00	-6.50E+00	0.00	-11.20	-4.70
14.0	0.00	1.00E-07	1.00E+00	-7.00E+00	0.00	-11.70	-4.70

Enter K_a	Enter $[HA]_T$
1.00E-07	2.00E-05

4. Lime (calcium hydroxide) is sometimes added to wastewater to reduce the phosphate concentration to acceptable levels. In a pilot study, 10.0 g of $Ca(OH)_2$ was dissolved in a 100. L sample of pH neutral water. Calculate the maximum total phosphate concentration $[PO_4^{3-}]_T$ that this test solution could contain assuming that the concentration of PO_4^{3-} is controlled by precipitation of calcium phosphate, $K_{sp} = 1.3 \times 10^{-32}$.

Solution: Calcium hydroxide is moderately soluble and will dissolve in water to yield Ca^{2+} and OH^- according to;

$$Ca(OH)_2(s) \rightarrow Ca^{2+}(aq) + 2\ OH^-(aq)$$

Since 10.0 g of calcium hydroxide is dissolved in 100. L, the resulting concentrations are;

$$[Ca^{2+}] = 10.0\ g/100.\ L \times 1\ mol/74.0\ g = 1.35 \times 10^{-3}\ mol/L$$

and

$$[OH^-] = 10.0\ g/100.\ L \times 1\ mol/74.0\ g \times 2\ mol\ OH^-/1\ mol\ Ca(OH)_2 = 2.70 \times 10^{-3}\ mol/L$$

Therefore the pOH = $-\log(2.70 \times 10^{-3}) = 2.57$
and pH = 11.43, $[H^+] = 3.71 \times 10^{-12}$ mol/L

Since the phosphate concentration is controlled by the precipitation of $Ca_3(PO_4)_2(s)$ (aka calcium phosphate), we can use the solubility product expression to solve for the $[PO_4^{3-}]$.

$$Ca_3(PO_4)_2(s) \ ==== \ 3\ Ca^{2+} + 2\ PO_4^{3-}$$

$$K_{sp} = [Ca^{2+}]^3 [PO_4^{3-}]^2 = 1.3 \times 10^{-32}$$

Rearranging and solving for yields;

$$[PO_4^{3-}] = \sqrt{\frac{1.3 \times 10^{-32}}{(1.35 \times 10^{-3})^3}} = 2.29 \times 10^{-12}\ mol/L$$

However, this is the concentration of just one of the forms of phosphate ion since;

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

Since at pH 11.4, it is fair to assume that $[H_3PO_4]$ and $[H_2PO_4^-] \sim 0$ (see further pKa's and/or pH speciation diagram).

We can simply the expression for total phosphate to;

$$[PO_4^{3-}]_T \cong [HPO_4^{2-}] + [PO_4^{3-}]$$

Since we have calculated $[PO_4^{3-}]$ above, we need to relate this to the concentration of $[HPO_4^{2-}]$ which we can accomplish using the K_{a3} expression;

$$K_{a3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]}$$

Rearranging to isolate $[HPO_4^{2-}]$ and substituting in the values for $[H^+]$ and K_{a3} (textbook) gives;

$$[HPO_4^{2-}] = \frac{[H^+][PO_4^{3-}]}{K_{a3}} = \frac{(3.71 \times 10^{-12})}{4.2 \times 10^{-13}}[PO_4^{3-}] = 8.85\ [PO_4^{3-}]$$

Therefore

$$[PO_4^{3-}]_T \cong [HPO_4^{2-}] + [PO_4^{3-}] = (8.85 + 1)\ [PO_4^{3-}]$$

Given that $[PO_4^{3-}] = 2.29 \times 10^{-12}$ mol/L (above), this yields $\mathbf{[PO_4^{3-}]_T = 2.26 \times 10^{-11}\ M}$

5. How is the solubility of FeS(s) in marine sediments expected to be affected by the pH and the [H_2S(aq)] in the surrounding pore water? Calculate the equilibrium concentration of Fe^{2+} (ppb) at pH 5 and pH 8, assuming the H_2S is 1.0 x 10^{-3} M. pK_{sp}(FeS) = +16.84.

$$\text{FeS(s)} + 2\,\text{H}^+\text{(aq)} \;====\; \text{Fe}^{2+}\text{(aq)} + \text{H}_2\text{S}$$

Solution: Examination of the equilibria, it is apparent that FeS becomes less soluble with increasing pH and increasing concentration of H_2S as predicted by Le Chatalier's Principle.

Writing the equilibrium expression for this reaction as;

$$K_{eq} = \frac{[Fe^{2+}][H_2S]}{[H^+]^2}$$

Since [H_2S] and [H^+] are known or can be determined, it appears that we could solve this problem provided we know the value of K_{eq}.

$$[Fe^{2+}] = \frac{K_{eq}\,[H^+]^2}{[H_2S]}$$

To calculate K_{eq}, we combine simpler chemical equilibria for which the equilibrium constants are known as follows;

$$\begin{array}{ll} \text{FeS(s)} \;====\; \text{Fe}^{2+} + \text{S}^{2-} & K_{sp} \\ \text{H}^+ + \text{S}^{2-} \;====\; \text{HS}^- & 1/K_{a2} \\ \underline{\text{H}^+ + \text{HS}^- \;====\; \text{H}_2\text{S}} & \underline{1/K_{a1}} \\ \text{FeS(s)} + 2\,\text{H}^+\text{(aq)} \;====\; \text{Fe}^{2+}\text{(aq)} + \text{H}_2\text{S} & \end{array}$$

$$K_{eq} = K_{sp}\,K_{a1}^{-1}\,K_{a2}^{-1}$$
$$= (10^{-16.84}) \text{ x } (10^{7.00}) \text{ x } (10^{11.96})$$
$$= 1.32 \text{ x } 10^{2}$$

Note: In the presence of H^+, the K_{eq} is ~ 10^{19} times greater than K_{sp}.

So at pH 5, where essentially all of the reduced sulfur is present as H_2S we have;

$$[Fe^{2+}] = \frac{K_{eq}\,[H^+]^2}{[H_2S]} = \frac{(1.32x10^{2})(10^{-5})^2}{(1.0x10^{-3})} = 1.32 \text{ x } 10^{-5} \text{ M}$$

Converting this to ppb as follows;

1.32 x 10^{-5} mol/L x 55.85 g/1 mol x 10^{6} μg/g x 1 L/1.00 kg = 737 μg/kg = **700 ppb**

Repeating this calculation at pH 8 requires a modification of the [H_2S] since only a fraction of the reduced sulfur will be present in this form (see Q3 above for α_{H2S} at pH 8).

$[H_2S] = \alpha_{H2S}$ x $[H_2S]_T$ = (0.091) (1.0 x 10^{-3} M) = 9.1 x 10^{-5} M

$$[Fe^{2+}] = \frac{K_{eq}\,[H^+]^2}{[H_2S]} = \frac{(1.32x10^{2})(10^{-8})^2}{(9.1x10^{-5})} = 1.45 \text{ x } 10^{-10} \text{ M}$$

Converting this to ppb as follows;

1.45 x 10^{-10} mol/L x 55.85 g/1 mol x 10^{6} μg/g x 1 L/1.00 kg = 8.10 x 10^{-3} μg/kg = **0.008 ppb**

Note; FeS(s) is roughly 10^5 times less soluble at pH 8 than pH 5 in the presence 10^{-3} M H_2S.

6. Using the pe-pH speciation diagrams for C, N and S predict the predominant form/s of each of these elements in Morrell Lake (pH = 8.1, ORP = 190 mV). Note, the ORP readings were measured using an internal silver/silver chloride reference electrode, whereas E_h values are referenced to a standard hydrogen electrode (SHE). Therefore, the following correction applies: Eh (vs SHE) V = ORP (vs Ag/AgCl) V + 0.220 V and pe = E_h/0.0591 (at 25°C)

Solution: First convert the measured ORP value to the corresponding pe using the information provided, i.e., pe = (0.190 + 0.220) V/ 0.0591 = 6.93
Using this pe and the pH = 8.1, locate the dominant species in the appropriate pe-pH speciation diagram (provided in the Course Reference package).

Under these conditions;
the dominant form of **Carbon is HCO_3^-**
the dominant form of **Nitrogen is NO_3^-**
the dominant form of **Sulfur is SO_4^{2-}**

7. a) Calculate the pe of oxygenated surface water (pH 8.1) in redox equilibrium with a dry atmosphere at sea level. What would you expect as the predominant forms for lead and chromium under these conditions?

Solution: To answer part a) we first need to establish the redox couple that will allow us to calculate the value of pe. Since the question states that the surface water is in redox equilibrium with a dry atmosphere, we use the O_2/H_2O redox couple and a P_{O2} = 0.21 atm (textbook).

Writing the reaction as a reduction;

$$O_2 + 4\,H^+ + 4\,e^- \;====\; 2\,H_2O \qquad E^o = 1.23\text{ V},\ pe^o = 20.8$$

Since we need the value of pe at non-standard state concentrations we must use;

$$pe = pe^o - (1/n)\log Q$$

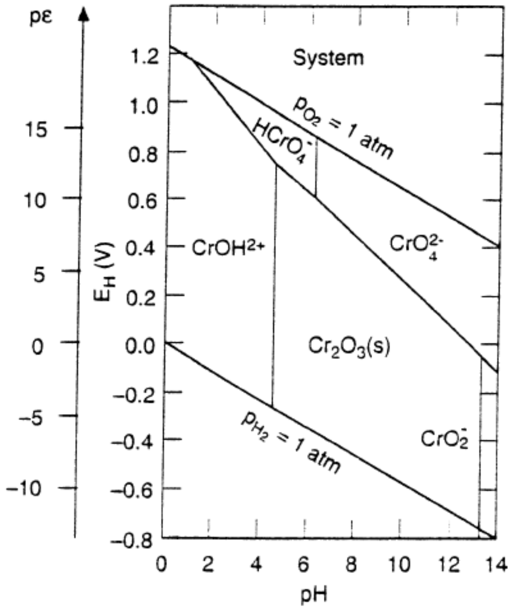
Substituting in for $[H^+]$ and P_{O2} we calculate;

$$pe = 20.8 - \left(\frac{1}{4}\right)\log\frac{1}{[H^+]^4 P_{O2}} = 20.8 - \left(\frac{1}{4}\right)\log\frac{1}{(10^{-8.1})^4(0.21)} = 20.8 - 8.2 = 12.5$$

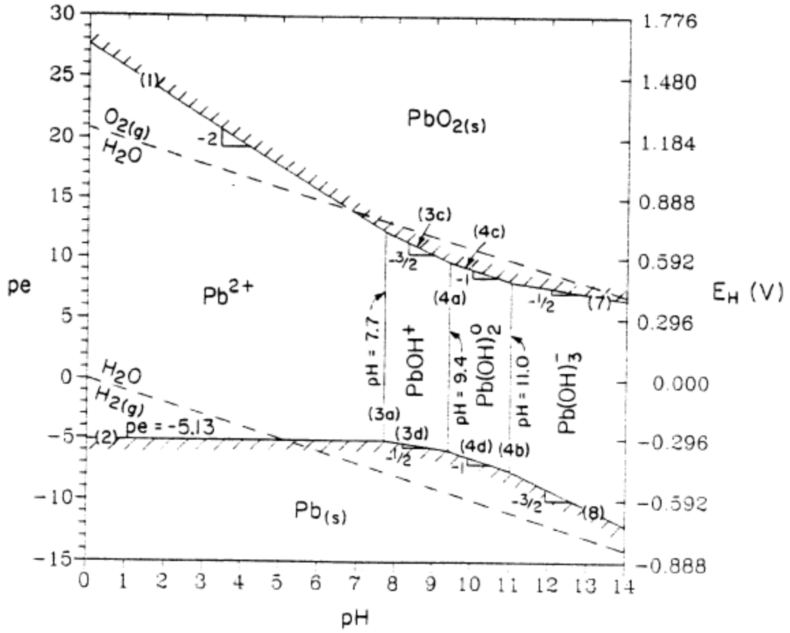
Now we can use pH 8.1 and pe 12.5 to identify the dominante species on the appropriate pe-pH diagram (see attached).

Therefore;
the dominant form/s of lead is PbO_2(s) or $PbOH^+$
the dominant form of chromium is CrO_4^{2-}

pH – pe Speciation Diagrams for Chromium and Lead at specified conditions



pε vs. pH diagram for Cr. [TOTCr] (dissolved) = 10^{-6} M 25°C.



pe-pH diagram for $Pb_T = 10^{-6}$ *M* at 25°C/1 atm obtained using "simplifying" assumptions regarding dissolved Pb(II) chemistry. "Simplifying" assumptions include: 1) $[Pb^{2+}] \simeq 10^{-6}$ *M* along boundarylines 1 and 2; 2) $[PbOH^+] \simeq 10^{-6}$ *M* along boundarylines 3c and 3d; 3) $[Pb(OH)_2^o] = 10^{-6}$ *M* along lines 4c and 4d; 4) $[Pb(OH)_3^-] \simeq 10^{-6}$ *M* along lines 7 and 8. (Note

b) Calculate the equation of the redox boundary between NO_3^-/NH_4^+ as a function of pH at 25°C and a $C_{species} = 0.10$ mM.

Solution: To do this we need the balanced half-reaction for the redox couple;

$$NO_3^- + 8\,e^- + 10\,H^+ \;====\; NH_4^+ + 3\,H_2O \qquad E^o = 0.882\text{ V},\ pe^o = 14.9$$

Using the general form of the equation to correct the pe for non-standard states;

$pe = pe^o - (1/n)\log Q$

we can make the appropriate substitutions and expand to separate out a $\log [H^+]^{-1}$ (i.e., pH) term. Doing so yields;

$$pe = 14.9 - \left(\frac{1}{8}\right)\log\frac{[NH_4^+]}{[H^+]^{10}[NO_3^-]} = 14.9 - \left(\frac{1}{8}\right)\log[H^+]^{-10} - \log\frac{[NH_4^+]}{[NO_3^-]}$$

$$= 14.9 - \left(\frac{10}{8}\right)pH - \left(\frac{1}{8}\right)\log\frac{[NH_4^+]}{[NO_3^-]}$$

Since at the redox boundary, $[NH_4^+] = [NO_3^-]$, the last term drops out of the equation and the boundary is given by;

$pe = 14.9 - (5/4)\,pH$

8. a) A solution at pH = 7.0 contains Mn^{2+} at an activity of 10^{-5}, as well as some $MnO_2(s)$. The redox half-cell reaction for the $Mn^{2+}/MnO_2(s)$ reaction is shown below. What is the pe of the solution, assuming the system is at equilibrium?

$$MnO_2(s) + 4\,H^+ + 2\,e^- \rightarrow Mn^{2+} + 2\,H_2O \qquad pe^o = 20.8$$

Solution: Once again we use;

$pe = pe^o - (1/n)\log Q = 20.8 - (1/2)\log([Mn^{2+}]/[H^+]^4)$

Since the activity of $Mn^{2+} = 10^{-5}$ and that of $H^+ = 10^{-7}$,
we calculate $pe = 20.8 - (1/2)\log(10^{-5}/(10^{-7})^4) = 20.8 - 11.5 = 9.3$

$\therefore$ pe = 9.3

b) What is the expected ratio of $[Fe^{2+}]/[Fe^{3+}]$ in this same solution?

Solution: The half reaction is given by;

$$Fe^{2+} + e- \;====\; Fe^{3+} \qquad E^o = 0.771\text{ V},\ pe^o = 13.0$$

So we can write;

$9.3 = pe^o - (1/n)\log Q = 13.0 - (1/1)\log([Fe^{2+}]/[Fe^{3+}])$

Thus,

$-\log([Fe^{2+}]/[Fe^{3+}]) = 9.3 - 13.0 = -3.7$

So;

$[Fe^{2+}]/[Fe^{3+}] = 10^{3.7} = 5.01 \times 10^3$