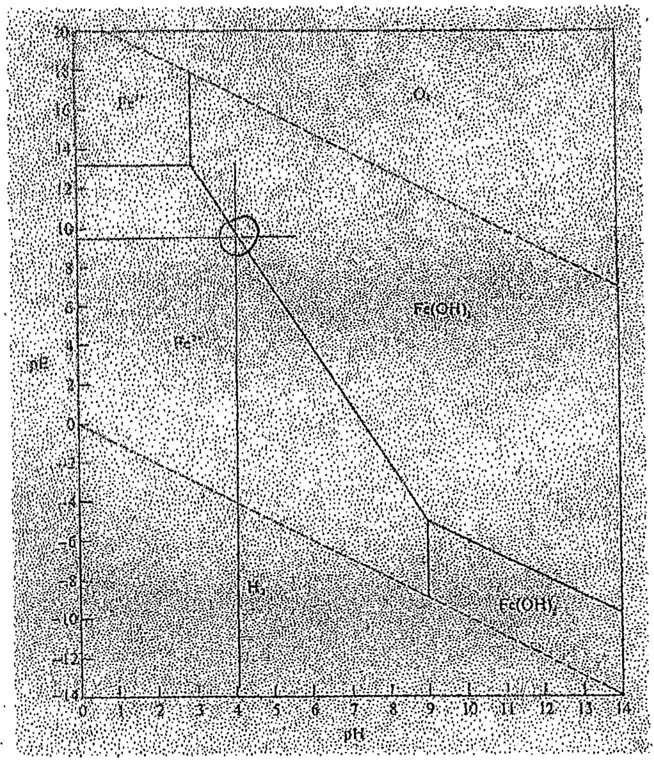
CHEM 301
Assignment #2

SOLUTIONS

1. A pond in an area affected by acid mine drainage is observed to have freshly precipitated **$Fe(OH)_3$**(s) at pH 4. What is the minimum value of p*e* in this water? Use the appropriate p*e*-pH speciation diagram to predict the dominant chemical speciation of carbon, sulfur and copper under these conditions.



We can use the pe-pH diagram for iron and read a minimum pe value of 9.5

In absense of further information we can assume the diagram has been constructed for $[Fe^{2+}] = 1M$ (which is not likely to be the conc in this sample).

If we are willing to assume a $[Fe^{2+}]$, then we could calculate a value of pe using

$$Fe(OH)_3(s) + 3H^+ + e^- \longrightarrow Fe^{2+} + 3H_2O$$

$$pe = pe^o - \frac{n_H}{n_e} pH - \log [Fe^{2+}]$$

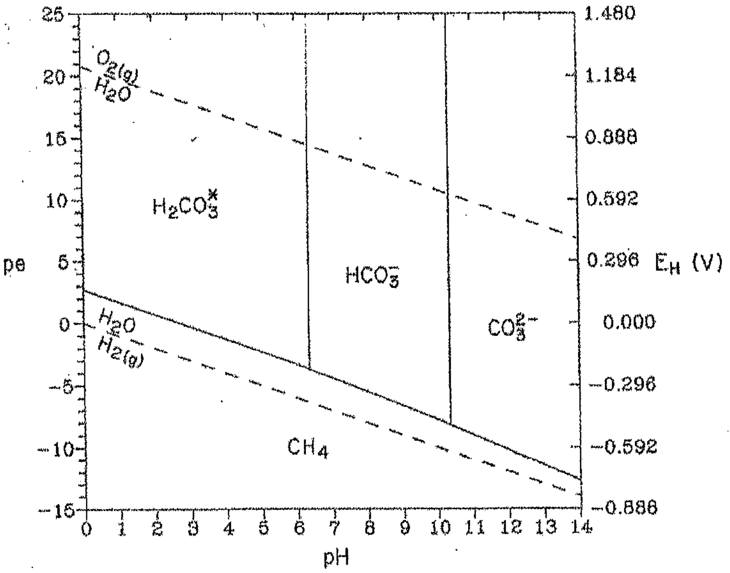


Figure 23.5 pe-pH diagram for aqueous carbon at 25°C/1 atm, and when solid elemental forms of carbon are not considered. Activity corrections are neglected. Since $H_2CO_3^*$, HCO_3^-, CO_3^{2-}, and CH_4 all contain one atom of carbon, and since no solid forms of carbon are considered, the diagram is independent of C_T. As the pe is lowered at any given pH value, the diagram indicates that CH_4 can become the dominant form of carbon before the in-situ p_{H_2} can reach 1 atm.

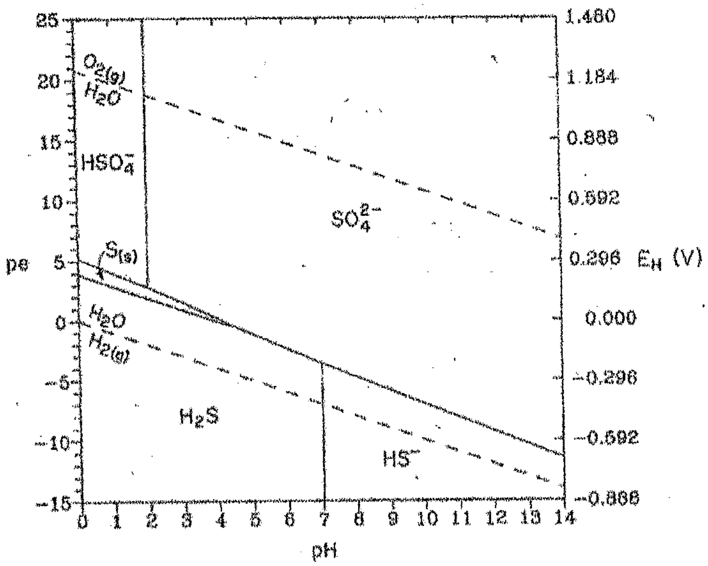


Figure 23.12 pe-pH diagram for aqueous sulfur when $S_T = 10^{-3}$ *M* and 25°C/1 atm. Activity corrections are neglected. $S_{(s)}$ is only possible at relatively low pH. As the pe is lowered at any given pH value, the diagram indicates that S(−II) (either as H_2S or as HS^-) can become the dominant form of sulfur before the in-situ p_{H_2} can reach 1 atm.

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

$$\mathbf{FeS(s)} \;+\; 2\,\mathbf{H^+(aq)} \;=\!=\!=\!=\; \mathbf{Fe^{2+}(aq)} \;+\; \mathbf{H_2S}$$

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;

$$\begin{array}{ll}
FeS(s) \;=\!=\!=\!=\; Fe^{2+} + S^{2-} & K_{sp} \\
H^+ + S^{2-} \;=\!=\!=\!=\; HS^- & 1/K_{a2} \\
\underline{H^+ + HS^- \;=\!=\!=\!=\; H_2S} & \underline{1/K_{a1}} \\
FeS(s) + 2\,H^+(aq) \;=\!=\!=\!=\; Fe^{2+}(aq) + H_2S & \\
 & K_{eq} = K_{sp}\,K_{a1}^{-1}\,K_{a2}^{-1} \\
 & = (10^{-16.84}) \times (10^{7.00}) \times (10^{11.96}) \\
 & = 1.32 \times 10^2
\end{array}$$

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;

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

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).

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

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

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.

3. Boric acid is a triprotic acid (**H_3BO_3**); $pK_{a1} = 9.24$, $pK_{a2} = 12.74$ and $pK_{a3} = 13.80$.

a) Derive an expression for the fractional abundance of **H_3BO_3** as a function of pH

b) Construct a fully labeled pH speciation diagram for boric acid over the pH range of 0 to 14 using Excel spreadsheet at a 0.2 pH unit interval.

***Strategy*:** We can write an expression for any triprotic acid as;

$$\alpha_{H3A} = \frac{[H_3A]}{[H_3A]_T} = \frac{[H_3A]}{[H_3A] + [H_2A^-] + [HA^{2-}] + [A^{3-}]}$$

Use acid dissociation equilibrium expressions for K_{a1}, K_{a2} and K_{a3} to make appropriate substitutions in the denominator that give $[H_3A]$ as a common factor.

Solution: a)

$$\alpha_{H_3BO_3} = \frac{[H_3BO_3]}{[H_3BO_3]_T} = \frac{[H_3BO_3]}{[H_3BO_3] + [H_2BO_3^-] + [HBO_3^{2-}] + [BO_3^{3-}]}$$

to derive an expression in terms of $[H^+]$
rearrange expressions for Ka_1, Ka_2 and Ka_3
and substitute

$$H_3BO_3 \rightleftharpoons H^+ + H_2BO_3^- \qquad Ka_1 = \frac{[H^+][H_2BO_3^-]}{[H_3BO_3]}$$

$$\therefore [H_2BO_3^-] = \frac{Ka_1 [H_3BO_3]}{[H^+]}$$

$$H_2BO_3^- \rightleftharpoons H^+ + HBO_3^{2-} \qquad Ka_2 = \frac{[H^+][HBO_3^{2-}]}{[H_2BO_3^-]}$$

$$\therefore [HBO_3^{2-}] = \frac{Ka_2 [H_2BO_3^-]}{[H^+]}$$

$$= \frac{Ka_1 Ka_2 [H_3BO_3]}{[H^+]^2}$$

$$HBO_3^{2-} \rightleftharpoons H^+ + BO_3^{3-} \qquad Ka_3 = \frac{[H^+][BO_3^{3-}]}{[HBO_3^{2-}]}$$

$$\therefore [BO_3^{3-}] = \frac{Ka_3 [HBO_3^{2-}]}{[H^+]}$$

$$= \frac{Ka_1 Ka_2 Ka_3 [H_3BO_3]}{[H^+]^3}$$

Therefore

$$\alpha_{H_3BO_3} = \frac{[H_3BO_3]}{[H_3BO_3] + \frac{Ka_1[H_3BO_3]}{[H^+]} + \frac{Ka_1Ka_2[H_3BO_3]}{[H^+]^2} + \frac{Ka_1Ka_2Ka_3[H_3BO_3]}{[H^+]^3}}$$

$$= \frac{1}{1 + \frac{Ka_1}{[H^+]} + \frac{Ka_1Ka_2}{[H^+]^2} + \frac{Ka_1Ka_2Ka_3}{[H^+]^3}}$$

$$= \frac{[H^+]^3}{[H^+]^3 + Ka_1[H^+]^2 + Ka_1Ka_2[H^+] + Ka_1Ka_2Ka_3}$$

set up Excel spreadsheet pKa_1; pKa_2, pKa_3

pH $[H^+]$ $\alpha_{H_3BO_3}$ $\alpha_{H_2BO_3^-}$ $\alpha_{HBO_3^{2-}}$ $\alpha_{BO_3^{3-}}$

plot x-y scatter plot, $\alpha_{H_3BO_3}$ vs pH

overlay $\bar{w}$

$\alpha_{H_2BO_3^-}$ vs pH

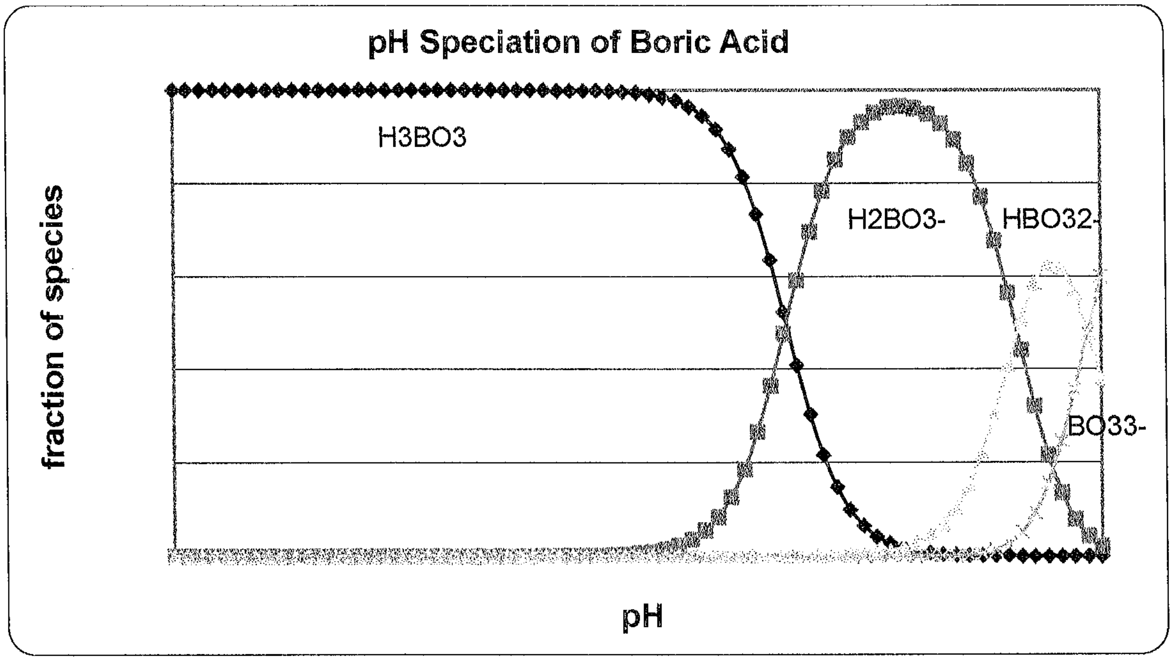
& $\alpha_{HBO_3^{2-}}$ vs pH

& $\alpha_{BO_3^{3-}}$ vs pH

b)

SPECIATION FOR THE BORIC ACID SYSTEM

		alpha	alpha	alpha	alpha			
pH	**[H+]**	**H_3BO_3**	**$H_2BO_3^-$**	**HBO_3^{2-}**	**BO_3^{3-}**	**Ka1**	**Ka2**	**Ka3**
0	1.000E+00	1.00E+00	5.75E-10	1.05E-22	1.65E-36			
0.2	6.310E-01	1.00E+00	9.11E-10	2.63E-22	6.58E-36			
0.4	3.981E-01	1.00E+00	1.44E-09	6.60E-22	2.62E-35			
0.6	2.512E-01	1.00E+00	2.29E-09	1.66E-21	1.04E-34			
0.8	1.585E-01	1.00E+00	3.63E-09	4.17E-21	4.15E-34			
1.0	1.000E-01	1.00E+00	5.75E-09	1.05E-20	1.65E-33	5.75E-10	1.82E-13	1.58E-14
1.2	6.310E-02	1.00E+00	9.11E-09	2.63E-20	6.58E-33			



4. At p**Cl**$^-$ = 2.0, **Cd**$^{2+}$ and **CdCl**$^+$ are the only dominant cadmium chloride species with a 50% fractional abundance of each.

a) Calculate the equilibrium constant for the formation of **CdCl**$^+$ (β_1).

b) Derive an expression for the fractional abundance of **CdCl**$^+$ as a function of [**Cl**$^-$] and $\beta_1 - \beta_4$ for cadmium chloro species.

c) Calculate the fractional abundance of **CdCl**$^+$ species at [**Cl**$^-$]$_{\text{seawater}}$.

Strategy: Use equilibrium expression for the various complexation states of Cd^{2+} and Cl$^-$ (i.e., $K_{f1} = \beta_1$).

Solution:

a) At pCl$^-$ = 2.0, [Cl$^-$] = 10^{-2} M and at this chloride ion concentration, we know that [Cd^{2+}] = [CdCl$^+$], since $\alpha_{Cd2+} = \alpha_{CdCl+} = 0.50$.

$$\beta_1 = \frac{[CdCl^+]}{[Cd^{2+}][Cl^-]} = \frac{1}{10^{-2}} = 100$$

b)

$$\alpha_{CdCl+} = \frac{[CdCl^+]}{[Cd^{2+}] + [CdCl^+] + [CdCl_2] + [CdCl_3^-] + [CdCl_4^{2-}]}$$

$$Cd^{2+} + Cl^- \rightleftharpoons CdCl^+ \quad \beta_1 = \frac{[CdCl^+]}{[Cd^{2+}][Cl^-]} \quad \therefore [Cd^{2+}] = \frac{[CdCl^+]}{\beta_1[Cl^-]}$$

$$Cd^{2+} + 2Cl^- \rightleftharpoons CdCl_2 \quad \beta_2 = \frac{[CdCl_2]}{[Cd^{2+}][Cl^-]^2} \quad \therefore [CdCl_2] = \beta_2[Cd^{2+}][Cl^-]^2$$

$$Cd^{2+} + 3Cl^- \rightleftharpoons CdCl_3^- \quad \beta_3 = \frac{[CdCl_3^-]}{[Cd^{2+}][Cl^-]^3} \quad \therefore [CdCl_3^-] = \beta_3[Cd^{2+}][Cl^-]^3$$

$$Cd^{2+} + 4Cl^- \rightleftharpoons CdCl_4^{2-} \quad \beta_4 = \frac{[CdCl_4^{2-}]}{[Cd^{2+}][Cl^-]^4} \quad \therefore [CdCl_4^{2-}] = \beta_4[Cd^{2+}][Cl^-]^4$$

Substituting in for $[Cd^{2+}] = [CdCl^+]/\beta_1[Cl^-]$ so all terms have common [CdCl$^+$] term.

Therefore,

$$[CdCl_2] = \frac{\beta_2 [CdCl^+][Cl^-]^2}{\beta_1 [Cl^-]} = \frac{\beta_2}{\beta_1} [CdCl^+][Cl^-]$$

$$[CdCl_3^-] = \frac{\beta_3 [CdCl^+][Cl^-]^3}{\beta_1 [Cl^-]} = \frac{\beta_3}{\beta_1} [CdCl^+][Cl^-]^2$$

$$[CdCl_4^{2-}] = \frac{\beta_4 [CdCl^+][Cl^-]^4}{\beta_1 [Cl^-]} = \frac{\beta_4}{\beta_1} [CdCl^+][Cl^-]^3$$

Thus,

$$\alpha_{CdCl^+} = \frac{[CdCl^+]}{\frac{[CdCl^+]}{\beta_1 [Cl^-]} + [CdCl^+] + \frac{\beta_2 [CdCl^+][Cl^-]}{\beta_1} + \frac{\beta_3 [CdCl^+][Cl^-]^2}{\beta_1} + \frac{\beta_4 [CdCl^+][Cl^-]^3}{\beta_1}}$$

$$= \frac{1}{\frac{1}{\beta_1 [Cl^-]} + 1 + \frac{\beta_2 [Cl^-]}{\beta_1} + \frac{\beta_3 [Cl^-]^2}{\beta_1} + \frac{\beta_4 [Cl^-]^3}{\beta_1}}$$

$$= \frac{\beta_1 [Cl^-]}{1 + \beta_1 [Cl^-] + \beta_2 [Cl^-]^2 + \beta_3 [Cl^-]^3 + \beta_4 [Cl^-]^4}$$

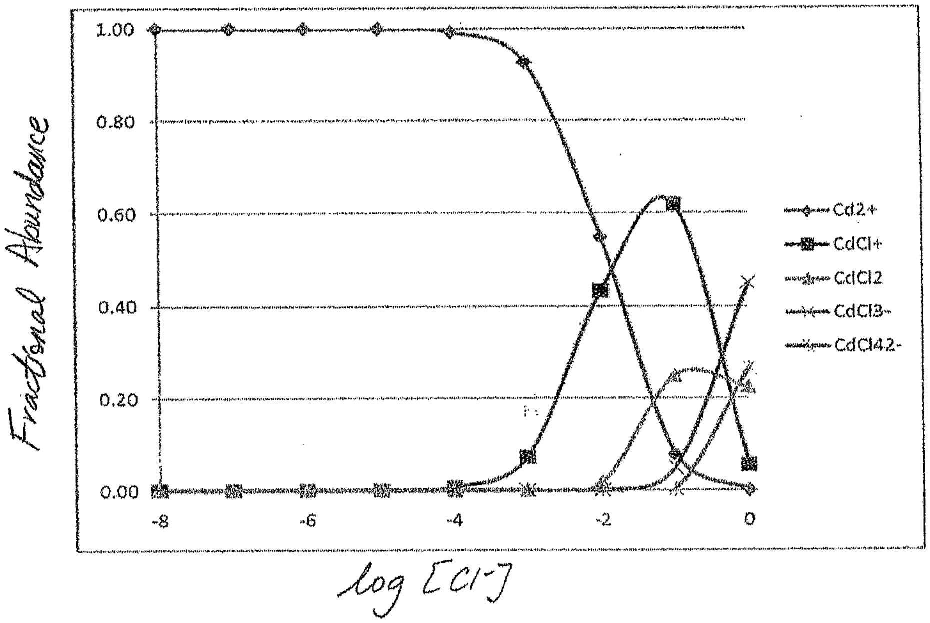
c) Seawater has a [Cl-] = 0.55 M, ~~thus~~ and

$$\left.\begin{aligned}\beta_1 &= 7.9\times10^1\\ \beta_2 &= 3.2\times10^2\\ \beta_3 &= 6.4\times10^2\\ \beta_4 &= 3.8\times10^2\end{aligned}\right\}\text{ from text Sec 10.1.2}$$

α_{CdCl+} =

$$= \frac{79(0.55)}{1+79(0.55)+3.2\times10^2(0.55)^2+6.4\times10^2(0.55)^3+3.8\times10^2(0.55)^4}$$

Speciation of Cadmium chloro species



$$= \frac{43.5}{1+43.5+96.8+106.5+34.8}$$

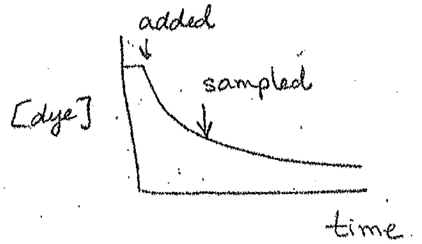
$$= 0.154 \longleftarrow \alpha_{CdCl^+}\text{ (seawater)}$$

5. To measure the volume of a small lake, you add 5.0L of a 2.0M solution of a non-toxic dye, which degrades by first order processes with a half-life of 3.0 days. After one week, in which the lake becomes well mixed, you take a 100. mL lake sample. The dye concentration in this sample is 2.9 x 10^{-6} M. Estimate the lake volume.

Strategy: The concentration of the dye is changing over time with a known half-life (i.e., system is not at steady-state). Since we know the total amount of dye added to the lake and the concentration after one week, we can use the integrated rate law (first order) to determine the initial concentration (assuming it is well mixed).

Solution:

amt dye added = 5.0L × 2.0M = 10. mols on day one



[dye] = 2.9×10^{-6} M one day seven

system is NOT at steady state
∴ use integrated rate law

$t_{1/2} = 3.0$ days $\quad \tau_p = \frac{t_{1/2}}{0.693} = 4.33$ days

$\therefore k = \frac{1}{\tau} = 0.231\ \text{day}^{-1}$

use integrated rate law to calculate $[\text{dye}]_0$ on day one

$$[C]_t = [C]_0 e^{-kt} \quad \therefore \quad [C]_0 = \frac{[C]_t}{e^{-kt}}$$

at $t = 7$ days, $[C]_7 = 2.9 \times 10^{-6}$ M

$$[\text{dye}]_0 = \frac{2.9 \times 10^{-6}\ M}{e^{-(0.231\ d^{-1})(7d)}} = 1.45 \times 10^{-5}\ M$$

Since $M \times V = \#\text{mols}$

$$\therefore V = \frac{\#\text{mols}}{M} = \frac{10.0\ \text{mols}}{1.45 \times 10^{-5}\ M}$$

$$= 6.9 \times 10^{5}\ L = 690\ m^3$$

6. 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 distilled 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, $K_{sp} = 1.3 \times 10^{-32}$.

Strategy: Use the solubility of $Ca_3(PO_4)_2$ and $[Ca^{2+}]$ to determine $[PO_4^{3-}]$. Then use pH to calculate other phosphate ions to yield $[PO_4]_T$.

Solution:

$$Ca_3(PO_4)_2\,(s) \rightleftharpoons 3\,Ca^{2+}_{(aq)} + 2\,PO_4^{3-}{}_{(aq)}$$

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

Since 10.0g of $Ca(OH)_2$ dissolved in 100. L

we have $[Ca^{2+}] = \dfrac{10.0\,g}{100.\,L} \times \dfrac{1\,mol}{74.1\,g} = 1.35 \times 10^{-3}\,\dfrac{mol}{L}$

and $[OH^-] = 2.70 \times 10^{-3}\,\dfrac{mol}{L}$

Therefore $pOH = 2.57$ and $pH = 11.43$.

If $[PO_4^{3-}]$ is controlled by solubility of $Ca_3(PO_4)_2$, then

$$[PO_4^{3-}] = \sqrt{\frac{K_{sp}}{[Ca^{2+}]^3}} = \sqrt{\frac{1.3 \times 10^{-32}}{(1.35 \times 10^{-3})^3}}$$

$$= 2.30 \times 10^{-12}\,\frac{mol}{L}$$

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

Since $pKa_1 = 2.15$, $pKa_2 = 7.20$, $pKa_3 = 12.38$

$\therefore$ at $pH = 11.43$, the only significant phosphate species are HPO_4^{2-} and PO_4^{3-}

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

Use Ka_3 to solve for $[HPO_4^{2-}]$ from $[PO_4^{3-}]$

$$Ka_3 = \frac{[PO_4^{3-}][H^+]}{[HPO_4^{2-}]} \quad \text{and} \quad [HPO_4^{2-}] = \frac{[PO_4^{3-}][H^+]}{Ka_3}$$

$$\therefore [HPO_4^{2-}] = \frac{(2.30 \times 10^{-12})(10^{-11.43})}{10^{-12.38}}$$

$$= 2.05 \times 10^{-11}$$

Therefore $[PO_4]_T = (2.05 \times 10^{-11} + 2.30 \times 10^{-12}) \frac{mol}{L}$

$$= 2.28 \times 10^{-11} \frac{mol}{L}$$

7. Water from the hypolimion of Maynard Lake has a measured pH of 5.81 and an ORP = -290 mV using an ORP probe with an internal silver/silver chloride reference electrode. Standard E_h values are referenced to a standard saturated hydrogen electrode (SHE). Look up the standard reduction potential for the **AgCl**(s) + e- → **Ag**(s) + **Cl^-** half reaction and correct the field ORP reading to E_h (mV).

a) Report the pe value of the sample.

b) Using the appropriate *pe*-pH (Pourbaix) diagrams, predict the dominant forms of chromium, and selenium.

Solution:

a) The E^o for the AgCl/Cl half reaction is given as 0.221 V vs SHE (textbook), therefore the measured ORP needs to be corrected to $E_h = E_{Ag/AgCl} + E_{ORP} = -0.290 + 0.221$ V = -0.068 V. So, pe = -0.068/0.0591 = **-1.15**

b) Depending on the particular Pourbaix diagrams used (see below), the dominant speciation at pH = 5.81 and pe = -1.15 are as follows.

Chromium: $CrOH^{2+}$

Selenium: Se(s) and HSe^-

Chromium

Cr-O-H Species Considered

Cr[2+], Cr[3+],
CrO_4[2-], Cr_2O_7[2-]
CrOH[2+], $HCrO_4$[-],
Cr(s), CrO_2(s),
CrO_3(s), Cr_2O_3(s),
Cr_3O_4(s), Cr_5O_{12}(s),
Cr_8O_{21}(s)

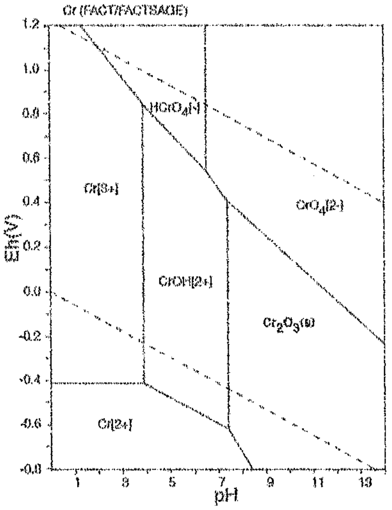


Figure 35: Eh-pH diagrams of the system Cr-O-H (1). $\sum Cr = 10^{-10}$, 298.15K, 10^5 Pa.

Selenium

Se-O-H Species Considered

SeO_4[2-], Se[2-],
SeO_3[2-], H_2Se(aq),
H_2SeO_3(aq), HSe[-],
$HSeO_3$[-], $HSeO_4$[-],
Se, Se_2O_5, SeO_2,
SeO_3

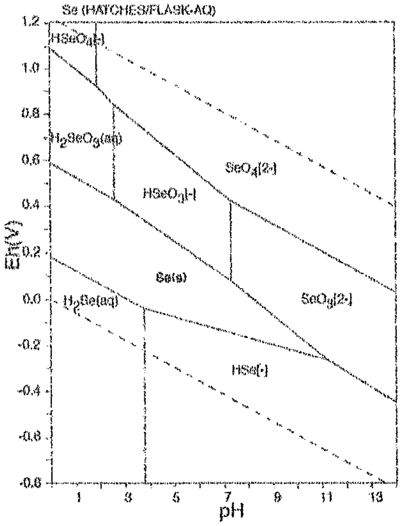


Figure 112: Eh-pH diagrams of the system Se-O-H (2). $\sum Se = 10^{-10}$, 298.15K, 10^5 Pa.

8. a) Calculate the *pe* of air saturated surface water at pH 8.1 in redox equilibrium with a dry atmosphere at sea level.

b) 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 **MnO**$_2$(s)/ **Mn**$^{2+}$ reaction is shown below. What is the pe of the solution, assuming the system is at redox equilibrium?

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

c) Determine the *pe* of redox boundary between **Fe(OH)**$_3$/**Fe**$^{2+}$ as a function of pH at 25°C and a total C_{Fe} = 0.010 mM.

a) Use O_2/H_2O redox couple

balanced half rxn : $O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \quad E^\circ = 1.23\,V$

$$\therefore pe = pe^\circ - \frac{n_H}{n_e}pH - \frac{1}{n_e}\log\frac{\{H_2O\}}{\{O_2\}}$$

$\{H_2O\}$ ← activity ≡ 1

$\{O_2\}$ ← fugacity ≅ 0.21

$$\text{So } pe = \frac{1.23}{0.0591} - \frac{4}{4}(8.1) - \frac{1}{4}\log\left(\frac{1}{0.21}\right)$$

$$= 20.8 - 8.1 - 0.17$$

$$pe = 12.5$$

b) $pe = pe^\circ - 2\,pH - \frac{1}{2}\log(10^{-5})$

$$= 20.8 - 14.0 - \tfrac{1}{2}(-5)$$

$$pe = 9.3$$

c) $Fe(OH)_3 + e^- + 3H^+ \rightarrow Fe^{2+} + 3H_2O$

$$pe = pe^\circ - \frac{3}{1}pH - \log(10^{-5}) = pe^\circ + 5 - 3\,pH$$

$$\text{where } pe^\circ = \frac{E^\circ}{0.0591} = \frac{-\Delta G^\circ/nF}{0.0591}$$

$$\text{and } \Delta G^\circ = \Sigma\,\Delta G^\circ_f(\text{pdts}) - \Sigma\,\Delta G^\circ_f(\text{react})$$

$$= [-78.9 + 3(-237)] - [-697] = -92.9\ \frac{kJ}{mol}$$

$$\therefore pe^\circ = 16.3,\ \text{So } pe = 21.3 - 3\,pH$$

9. The potentially fatal effects of acute arsenic exposure are well known, but in recent years the effects of long term low level (chronic) exposures has been hotly debated. As a consequence, the US EPA has recommended lowering the maximum contaminant level (MCL) from 50 ppb As to 5 ppb. Arsenic occurs naturally in two oxidation states: **As** (III) and **As** (V). It is acidic in both oxidation states, but much more so as **As**(V), in which case it is chemically similar to phosphoric acid [i.e., **P**(V)]. The pK_a values of arsenous acid, $\mathbf{H_3AsO_3}$ and arsenic acid, $\mathbf{H_3AsO_4}$ are shown below and indicate that most of the $\mathbf{H_3AsO_3}$ remains fully protonated at pH 7, whereas $\mathbf{H_3AsO_4}$ is extensively deprotonated. Because of this difference in ionic charge on the dominant species, it is easier to remove **As** (V) than **As** (III) from solution by adsorption and ion-exchange processes that might be employed at a water treatment plant.

$$\mathbf{AsO_4^{3-} + 2\,H^+ + 2\,e^- \rightarrow AsO_3^{3-} + H_2O} \qquad pe^\circ = 2.64$$

	pK_{a1}	pK_{a2}	pK_{a3}
$\mathbf{H_3AsO_3}$	9.23	12.10	13.41
$\mathbf{H_3AsO_4}$	2.24	6.76	11.60

Workers at a water treatment plant want to ensure that > 99% of the total arsenic $[As]_T$ in the water is in the oxidized form prior to feeding it to an ion-exchange process. If the pH of the water is 7.6, what is the minimum *pe* required for the treatment process to work?

Strategy: Identify the relevant redox couple at pH 7.6 and calculate the pe when [As(v)]/[As(III)] > 100.

The redox couple is $HAsO_4^{2-}$ / H_3AsO_3 since these are the dominant species at pH = 7.6

$$HAsO_4^{2-} + 2e^- + 4H^+ \longrightarrow H_3AsO_3 + H_2O$$

$$\therefore\ pe = pe^\circ - \frac{n_H}{n_e}\,pH - \frac{1}{n_e}\log\frac{[H_3AsO_3]}{[HAsO_4^{2-}]}$$

$$= pe^\circ - \frac{4}{2}\,pH - \frac{1}{2}\log\frac{1}{100}$$

$$= pe^\circ - 2pH - (\tfrac{1}{2})(-2.0)$$

$$= pe^\circ - 2(7.6) + 1$$

$$= pe^\circ - 14.2$$

Now we need to determine the value of pe°

Combing the following reactions

$\log K = 2(2.64)$ $= 5.28$	$AsO_4^{3-} + 2H^+ + 2e^- \longrightarrow AsO_3^{3-} + H_2O$	$pe^\circ = 2.64$
$\log \frac{1}{Ka_1 Ka_2 Ka_3}$ $= 34.7$	$AsO_3^{3-} + 3H^+ \longrightarrow H_3AsO_3$	$\frac{1}{Ka_1 Ka_2 Ka_3 (H_3AsO_3)}$
$\log Ka_3 (H_3AsO_4)$ $= -11.60$	$HAsO_4^{2-} \longrightarrow H^+ + AsO_4^{3-}$	$Ka_3 (H_3AsO_4)$

$$HAsO_4^{2-} + 4H^+ + 2e^- \longrightarrow H_3AsO_3 + H_2O$$

$$\log K_{eq} = 5.28 + 34.7 - 11.60 = 28.4$$

$$pe^\circ = \frac{1}{n_e} \log K_{eq} = \frac{1}{2}(28.4) = 14.2$$

Therefore,

$$pe = 14.2 - 14.2 = 0$$

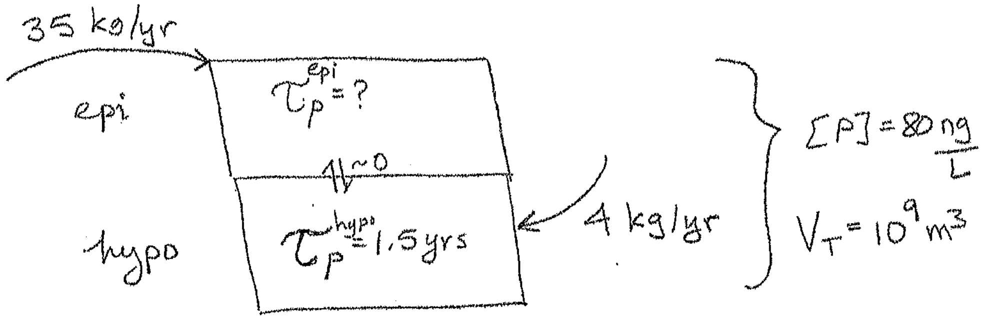
i.e., as long the pe of the water is maintained at $pe > 0$, then more than 99% of the arsenic species will be in the oxidized (+V) (arsenate) form.

10. A pollutant enters a thermally stratified lake by two distinct pathways. A river delivers the pollutant into the epilimnion at a rate of 35 kg/yr, whereas groundwater seepage delivers the pollutant to the hypoliminion at 4 kg/yr. Because of sedimentation, the residence time of the pollutant in the lower layer is 1.5 yrs. The average concentration in the whole lake is 80 ng/L, the total volume is 10^9 m^3 and everything is at steady state.

a) Draw a diagram of the system illustrating stocks and fluxes, where possible.
b) What is the total amount of pollutant in the lake?
c) Set up equations relating stocks, flows and residence times.
d) Solve for the residence time of the pollutant in the epilimnion (upper layer)?

Strategy:

Solution:



more information given for hypolimnion
∴ start here

$$\tau_p^{hypo} = \frac{\text{stock}}{\text{flux}}$$

↗ 1.5 yr ↑ 4. kg/yr

$$\therefore \text{stock} = \tau_p \cdot \text{flux} = (1.5 yr)(4. kg/yr) = 6 kg$$

$$V_T = V_{epi} + V_{hypo} = 10^9 m^3$$

$$\underset{\uparrow}{\text{stock}_T} = \text{stock(epi)} + \text{stock(hypo)}$$

$$\left(80 \frac{ng}{L}\right)\left(10^9 m^3\right)\left(\frac{10^3 L}{1 m^3}\right)\left(\frac{1 kg}{10^{12} ng}\right) = 80 kg$$

$$\therefore \text{stock (epi)} = 80 - 6 = 74 kg$$

$$\text{So } \tau_p^{epi} = \frac{74 kg}{35 kg/yr} = 2.1 yrs$$