1. Buffers (25%)

You have prepared a 10 mM phosphate buffer designed to hold pH at 8.1 (25°C, assume I~0). The two chemicals at your disposal are Na₂HPO₄ and KH₂PO₄.

A. How much of each compound (in mM concentration) would you add to create your buffer?

B. If you were to elevate the solution pH to 12.0, how much NaOH would you need to add (again in mM)?

A. This is a good use for the empirical Henderson Hasselbach Equation

\[ \text{pH} = pK_a + \log \frac{C_A}{C_{HA}} \]

Where \( C_A \) is the Na₂HPO₄ and \( C_{HA} \) is the KH₂PO₄

\[ \frac{C_A}{C_{HA}} = 10^{pH-pK_a} = 10^{8.1-7.2} = 7.943 \]

And since \( C_A + C_{HA} = 10 \text{ mM} \),

\[ \frac{C_A}{0.010-C_A} = 7.943 \]
\[ C_A = 0.07943 - 7.943C_A \]
\[ 8.943C_A = 0.07943 \]
\[ C_A = 0.00888M = \text{Na}_2\text{HPO}_4 \]
\[ C_{HA} = 0.00112M = \text{KH}_2\text{PO}_4 \]

B. Now determine the new mixture at pH 12 and determine amount of protons that need to be neutralized, but this time we’re closer to the third \( K_a \), so \( C_A \) is PO₄³⁻ and \( C_{HA} \) is HPO₄²⁻.
\[
\frac{C_A}{C_{HA}} = 10^{pH-pK_A} = 10^{12.0-12.3} = 0.501 \\
\frac{C_A}{0.010-C_A} = 0.501 \\
C_A = 0.00501 - 0.501C_A \\
1.501C_A = 0.00501 \\
C_A = 0.00334M = PO_4^{3-} \\
C_{HA} = 0.00666M = HPO_4^{2-}
\]

So the change in protons is:
\[
\Delta H^+ \text{ in Phosphates} = 2*0.00122+0.00888-0.00666 = 0.00466M \text{ or } 4.66\text{mM}
\]

But you also have significant hydroxide in the amount of \(10^{-2}\text{M or 10 mM}\). Therefore the overall hydroxide addition must be equal to the sum or:

\[
\text{NaOH dose} = 0.010+0.00466 = 0.01466M \text{ or } 14.66\text{mM}
\]

2. **Redox (25%)**

Sulfide and sulfate are two forms of sulfur that commonly exist in the aquatic environment. They often are found in groundwaters with both reduced and oxidized iron.

A. Write a balanced equation for the oxidation of hydrogen sulfide (HS\(^-\)) to sulfate by reaction with amorphous ferric hydroxide, liberating free ferrous iron.

B. Determine the net cell potential (\(E_{net}^o\)) and the equilibrium constant for this reaction and comment on what thermodynamics tells you about whether this is a favorable reaction in a typical groundwater and surface water systems.

C. At what pH does the equilibrium rest half-way between the two sulfur species? Assume a free ferrous iron concentration of 0.56 mg/L. Which species (sulfate or bisulfide) will predominate at lower pHs?

So we use redox #1 and #14, but we need to reverse #14 and cut its stoichiometry by a factor of 2 so that the electrons balance.

\begin{align*}
14 & \quad \text{Fe(OH)}_{3(am)} + 3H^+ + e^- = \text{Fe}^{2+} + 3\text{H}_2\text{O} \quad +0.95 \\
15 & \quad \text{SO}_4^{2-} + 9H^+ + 8e^- = \text{HS}^- + 4\text{H}_2\text{O} \quad +0.25
\end{align*}

This requires that we reverse the sign on the \(\Delta E^o\), but since the potentials are expressed on a per-electron basis, the change in stoichiometric factors doesn’t result in any additional change in \(\Delta E^o\).

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>Red</td>
<td>8Fe(OH)(_{3(am)}) + 24H(^+) + 8 e(^-) = 8 Fe(^{2+}) + 24H(_2)O</td>
<td>+0.95</td>
<td></td>
</tr>
<tr>
<td>Ox</td>
<td>HS(^-) + 4H(_2)O = SO(_4^{2-}) + 9 H(^+) + 8e(^-)</td>
<td>-0.25</td>
<td></td>
</tr>
<tr>
<td>Net</td>
<td>8Fe(OH)(_{3(am)}) + 15H(^+) + HS(^-) = 8 Fe(^{2+}) + SO(_4^{2-}) + 20H(_2)O</td>
<td>+0.70</td>
<td></td>
</tr>
</tbody>
</table>
\[ \log K = \frac{n}{0.059} E_{net}^0 \]
\[ = \frac{8}{0.059} (0.70) \]
\[ = 94.9 \]

\[ 10^{-94.9} = \frac{[Fe^{+2}]^8[SO_4^{2-}]}{[H^+]^{15}[HS^-]} \]

Now substituting in for $10^{-5}$M $Fe^{+2}$ (0.56 mg/L) we get:

\[ 10^{-94.9} = \frac{[10^{-5}]^8[SO_4^{2-}]}{[H^+]^{15}[HS^-]} \]
\[ \frac{[SO_4^{2-}]}{[HS^-]} = 10^{134.9} [H^+]^{15} \]

So when the quotient on the left is unity, the pH must be $134.9/15$ or 9.0. Below this pH sulfate will predominate and above it will be bisulfide.
3. Solubility (50%)

Ferrous Sulfide (Trollite, a form of Pyrrhotite) is a rather insoluble mineral with a \( K_{sp} \) of about \( 10^{-18.1} \). One would expect this to form in reduced groundwaters and sediments where ferrous iron and sulfide are major forms of Fe and S. \( \text{Fe(OH)}_2(s) \) would, of course, form under the right conditions as well.

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>pK</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{FeS}(s) = \text{Fe}^{2+} + \text{S}^2^- )</td>
<td>18.1</td>
</tr>
<tr>
<td>2</td>
<td>( \text{Fe(OH)}_2(s) + 2\text{H}^+ = \text{Fe}^{2+} + 2\text{H}_2\text{O} )</td>
<td>-12.9</td>
</tr>
<tr>
<td>3</td>
<td>( \text{FeOH}^+ + \text{H}^+ = \text{Fe}^{2+} + \text{H}_2\text{O} )</td>
<td>-9.5</td>
</tr>
<tr>
<td>4</td>
<td>( \text{Fe(OH)}_3^0 + 2\text{H}^+ = \text{Fe}^{2+} + 2\text{H}_2\text{O} )</td>
<td>-20.6</td>
</tr>
<tr>
<td>5</td>
<td>( \text{Fe(OH)}_3^- + 3\text{H}^+ = \text{Fe}^{2+} + 3\text{H}_2\text{O} )</td>
<td>-31.0</td>
</tr>
</tbody>
</table>

A. Prepare a combined Ferrous Hydroxide and Ferrous Sulfide solubility diagram assuming you have a total sulfide concentration of \( 10^{-6} \text{M} \). The x-axis should be pH and the y-axis should be log concentration. Show lines for the four soluble iron species based on each precipitate. Identify the key precipitation zones with FeT lines.

B. At what pH can both precipitates co-exist?

C. If the sulfide concentration was to increase, would the pH where the precipitates co-exist increase or decrease?

D. Describe in qualitative terms how the presence of \( 10^{-3} \text{M} \) total carbonate would affect the hydroxide and sulfide precipitation zones.

E. Describe in qualitative terms how the presence of \( 10^{-6} \text{M} \) mercury would affect the hydroxide and sulfide precipitation zones.

**Development of hydroxide solubility diagram**

a. Using the equilibria for ferric hydroxide from above:

\[
K = \frac{\left[\text{Fe}^{3+}\right]}{\left[\text{H}^+\right]^2} = 10^{+12.9}
\]

we get the following for the free aquo ion:

\[
\log[\text{Fe}^{2+}] = +12.9 - 2pH
\]

From this we use the hydroxide equilibria to get hydroxide species concentrations:

and for the monohydroxide:

---

1 Because of uncertainty over \( K_2 \) for the sulfide system, this equilibrium is often expressed in terms of \( \text{HS}^- \) rather than \( S^- \). However, to be consistent, I have converted it to the more conventional \( K_{so} \) form in a way that is internally consistent with our value of \( 10^{-13.9} \) for the sulfide \( K_2 \). These pK values were taken from Morel & Hering, 1993.
\[ K = \frac{[Fe^{+2}]}{[FeOH^+][H^+]} = 10^{+9.5} \]
\[ \log[FeOH^+] = -9.5 + \log[Fe^{+2}] - \log[H^+] \]
\[ \log[FeOH^+] = -9.5 + \log[Fe^{+2}] + pH \]
\[ \log[FeOH^+] = -9.5 + (12.9 - 2 pH) + pH \]
\[ \log[FeOH^+] = +3.4 - pH \]

now for the dihydroxide:

\[ K = \frac{[Fe^{+2}]}{[Fe(OH)_{2}^+][H^+]^2} = 10^{+20.6} \]
\[ \log[Fe(OH)_{2}^+] = -20.6 + \log[Fe^{+2}] - 2 \log[H^+] \]
\[ \log[Fe(OH)_{2}^+] = -20.6 + (12.9 - 2 pH) + 2 pH \]
\[ \log[Fe(OH)_{2}^+] = -7.7 \]

now for the trihydroxide:

\[ K = \frac{[Fe^{+2}]}{[Fe(OH)_{3}^+][H^+]^3} = 10^{+31.0} \]
\[ \log[Fe(OH)_{3}^+] = -31.0 + \log[Fe^{+2}] - 3 \log[H^+] \]
\[ \log[Fe(OH)_{3}^+] = -31.0 + (12.9 - 2 pH) + 3 pH \]
\[ \log[Fe(OH)_{3}^+] = -18.1 + pH \]
Development of Sulfide-based lines

b. Using the solubility product constant for ferrous sulfide from above:

\[ K = [Fe^{2+}] [S^{-2}] = 10^{-18.1} \]

b1. we get the following for the free aquo ion:

\[ \log[Fe^{2+}] = -18.1 - \log[S^{-2}] \]

\[ \log[Fe^{2+}] = -18.1 - \log[S_{r}] - \log \alpha_{2} \]

And for \(10^{-6}\) M total sulfides:

\[ \log[Fe^{2+}] = -18.1 - \log[10^{-6}] - \log \alpha_{2} \]

\[ \log[Fe^{2+}] = -12.1 - \log \alpha_{2} \]
For Sulfide Calculations:

\[
\alpha_2 = \frac{1}{K_1K_2} \left( \frac{[H^+]}{[H^+]^2} + \frac{1}{K_2} \right)
\]

For pH<7.02, \( \alpha_2 \approx \frac{K_1K_2}{[H^+]^2} \), or \( \log \alpha_2 \approx -20.92 + 2pH \)

For pH=7.02-13.9, \( \alpha_2 \approx \frac{K_2}{[H^+]^2} \), or \( \log \alpha_2 \approx -13.9 + pH \)

For pH>13.9, \( \alpha_2 \approx 1 \), or \( \log \alpha_2 \approx 0 \)

So for pH<7.02, we have:

\[
\log[Fe^{2+}] = -12.1 - (-20.92 + 2pH)
\]

\[
\log[Fe^{3+}] = 8.82 - 2pH, \quad @pH<7.02
\]

And for pH=7.02-13.9, we have:

\[
\log[Fe^{2+}] = -12.1 - (-13.9 + pH)
\]

\[
\log[Fe^{3+}] = +1.8 - pH, \quad @pH=7.02-13.9
\]

And for pH>13.9, we have:

\[
\log[Fe^{2+}] = -12.1 - (0)
\]

\[
\log[Fe^{3+}] = -12.1, \quad @pH>13.9
\]

b2. and for the monohydroxide:

from the Fe(OH)\(_2\)\(_{iso}\) based calculations, we know that:

\[
\log[Fe^{2+}] = -9.5 + \log[Fe^{2+}] + pH
\]

And now substituting in the FeS\(_{iso}\)-based free iron equation for pH<7.02, we have:

\[
\log[Fe^{2+}] = -9.5 + (8.82 - 2pH) + pH
\]

\[
\log[Fe^{3+}] = -0.68 - pH, \quad @pH<7.02
\]

And for pH=7.02-13.9, we have:

\[
\log[Fe^{2+}] = -9.5 + (1.8 - pH) + pH
\]

\[
\log[Fe^{3+}] = -7.7, \quad @pH=7.02-13.9
\]

And for pH>13.9, we have:

\[
\log[Fe^{2+}] = -9.5 + (-12.1) + pH
\]

\[
\log[Fe^{3+}] = -21.6 + pH, \quad @pH>13.9
\]

b3. now for the dihydroxide:
from the Fe(OH)$_{2(\text{aq})}$-based calculations, we know that:

$$\log[Fe(OH)_2^{\text{s}}] = -20.6 + \log[Fe^{2+}] - 2\log[H^+]$$

And now substituting in the FeS$_{1(\text{aq})}$-based FeOH equation for pH<7.02, we have:

$$\log[Fe(OH)_2^{\text{s}}] = -20.6 + (8.82 - 2pH) + 2pH$$

$$\log[Fe(OH)_2^{\text{s}}] = -11.78, \text{ @pH<7.02}$$

And for pH=7.02-13.9, we have:

$$\log[Fe(OH)_2^{\text{s}}] = -20.6 + (1.8 - pH) + 2pH$$

$$\log[Fe(OH)_2^{\text{s}}] = -18.8 + pH, \text{ @pH=7.02-13.9}$$

And for pH>13.9, we have:

$$\log[Fe(OH)_2^{\text{s}}] = -20.6 + (-12.1) + 2pH$$

$$\log[Fe(OH)_2^{\text{s}}] = -32.7 + 2pH, \text{ @pH>13.9}$$

B4. now for the trihydroxide:

from the Fe(OH)$_{2(\text{aq})}$-based calculations, we know that:

$$\log[Fe(OH)_3^{\text{s}}] = -31.0 + \log[Fe^{2+}] - 3\log[H^+]$$

$$\log[Fe(OH)_3^{\text{s}}] = -31.0 + \log[Fe^{2+}] + 3pH$$

And now substituting in the FeS$_{1(\text{aq})}$ based Fe(OH)$_2$ equation for pH<7.02, we have:

$$\log[Fe(OH)_3^{\text{s}}] = -31.0 + (8.82 - 2pH) + 3pH$$

$$\log[Fe(OH)_3^{\text{s}}] = -22.18 + pH, \text{ @pH<7.02}$$

And for pH=7.02-13.9, we have:

$$\log[Fe(OH)_3^{\text{s}}] = -31.0 + (1.8 - pH) + 3pH$$

$$\log[Fe(OH)_3^{\text{s}}] = -29.2 + 2pH, \text{ @pH=7.02-13.9}$$

And for pH>13.9, we have:

$$\log[Fe(OH)_3^{\text{s}}] = -31.0 + (-12.1) + 3pH$$

$$\log[Fe(OH)_3^{\text{s}}] = -43.1 + 3pH, \text{ @pH>13.9}$$
Red lines are based on sulfide solubility and black are based on hydroxide.
Now combining, we find that the hydroxide controls at pHs of 11.15 and above. Below this level, the carbonate is less soluble.

A. (30 points) see above

B. (5 points) The co-exist at a pH of about 11.1

C. (5 points) pH increases; it forms over a wider pH range

D. (5 points) it forms a 3rd solid phase (FeCO₃) which would infringe on the FeSₐ zone mostly

E. (5 points) it would precipitate HgS quite extensively, depressing the sulfide concentrations and thereby diminish the FeSₐ zone, allowing Fe(OH)₂ₐ to expand into lower pHs.
4. **Predominance (50%) Answer this or #3, your choice**

Lead carbonate (PbCO$_3$(s)) and red Lead Oxide (PbO$_2$(s)) are two important solid phases that may control lead solubility in water$^2$. In the attached pages is a detailed solution leading to a zinc hydroxide solubility diagram. Please use this to help solve the following problems.

A. Prepare a solubility diagram (log C vs pH) for a water that is potentially in equilibrium with lead hydroxide and lead carbonate. Assume the water has $10^{-3}$ M total carbonates (i.e., 1 mM C$_T$). Show all soluble species along with the Pb$_T$ line and indicate where precipitation will occur and the type of precipitate. To help you, there is a full solubility diagram for lead hydroxide only below. Feel free to work from this to prepare the combined carbonate-hydroxide diagram.

B. Below is a partially completed predominance diagram for the lead oxide – lead carbonate system. This was prepared for a total soluble lead concentration of $10^{-4}$ M (i.e., 0.1 mM Pb$_T$). Please complete this diagram showing the line(s) separating the two precipitates (C lines) and also determine and show the last remaining B line that separates the PbCO$_3$ precipitation zone from the Pb(OH)$_3$ zone (no precipitate). Show your work.

Stumm & Morgan Present the following data in Table A6.1

<table>
<thead>
<tr>
<th></th>
<th>OH$^-$</th>
<th>CO$_3^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb$^{2+}$</td>
<td>PbL</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>PbL$_2$</td>
<td>10.9</td>
</tr>
<tr>
<td></td>
<td>PbL$_3$</td>
<td>13.9</td>
</tr>
<tr>
<td></td>
<td>PbL$_2$$^-$</td>
<td>15.3</td>
</tr>
<tr>
<td></td>
<td>PbL • s</td>
<td>13.1</td>
</tr>
</tbody>
</table>

They note that the numerical values are Log formation constants.

Using these data you can rearrange the equilibrium quotients to get the following:

In equilibrium with PbO(s):

- Log[Pb$^{2+}$] = +12.7 -2pH
- Log[PbOH$^+$] = +5.0 -pH
- Log[Pb(OH)$_2$] = -4.4
- Log [Pb(OH)$_3$] = -15.4 +pH

2 Some mixed carbonate-hydroxide species may, in fact, be the most important, but they will not be considered here for the purpose of simplicity.
In equilibrium with PbCO$_3$(s):

- $\log[Pb^{2+}] = -13.1 - \log[CO_3^{2-}]$
- $\log[PbOH^+] = -20.8 + pH - \log[CO_3^{2-}]$
- $\log[Pb(OH)_2] = -30.2 + 2pH - \log[CO_3^{2-}]$
- $\log[Pb(OH)_3] = -41.2 + 3pH - \log[CO_3^{2-}]$
Answer to A.1.
Answer to A.2.

**Type A lines**

First, let's consider the boundary between the aquo ion and the monohydroxide (line A1)

At this point the two are equal, so we can take both equations and set them equal:
\[
\log[\text{Pb}^{+2}] = \log[\text{PbOH}^+] \\
+12.7 -2pH = +5.0 \quad -pH \\
pH = 12.7 - 5.0 \\
pH = 7.7
\]

following the same approach, we get the remaining A lines

A2:

\[
\log[\text{PbOH}^+] = \log[\text{Pb(OH)}_2] \\
+5.0 -pH = -4.4 \\
pH = 5.0 +4.4 \\
pH = 9.4
\]

A3:

\[
\log[\text{Pb(OH)}_2] = \log[\text{Pb(OH)}_3] \\
-4.4 = -15.4 +pH \\
pH = -4.4 + 15.4 \\
pH = 11.0
\]
Type B lines

First let’s examine the hydroxide equilibria. By looking at the PbO solubility graph, it appears that only free lead (Pb^{2+}) and the trihydroxide (Pb(OH)_3^-) are the dominant soluble species in equilibrium with the hydroxide precipitate at a total soluble lead concentration of 10^{-4} M.
So, first let’s look at the Pb$^{2+}$/PbOH$^+$ precipitate boundary. From the solubility product equation:

$$\log[\text{PbOH}^+] = +5.0 - \text{pH}$$

And presuming that this soluble species is the dominant one at the onset of precipitation, we set the concentration equal to the $\text{Me}_T = 10^{-4}\text{M}$:

$$-4 = +5.0 - \text{pH}$$

$$\text{pH} = 9$$

this is in the range where the monohydroxide predominates, so our assumption is correct.

B2:

Now let’s look at the Pb(OH)$_3$/PbO precipitate boundary. From the given solubility calculations, we have:

$$\log[\text{Pb(OH)}_3] = -15.4 + \text{pH}$$

And presuming that this soluble species is the dominant one at the onset of precipitation, we set the concentration equal to the $\text{Me}_T = 10^{-4}\text{M}$:

$$-4 = -15.4 + \text{pH}$$

$$\text{pH} = 11.4$$

This falls beyond the $\text{A3}$ line, so we’re in the Pb(OH)$_3$ zone, and the line is valid.
Inspection of the carbonate/hydroxide solubility diagram leads one to conclude that free lead may be the only soluble species that needs to be considered for the B lines defining carbonate solubility.

**B3**

So, lets look at the $\text{Pb}^{+2}/\text{PbCO}_3$ boundary: We may need to develop as many as three line segments due to carbonate’s pH dependence.:
Now looking at the given equilibrium expression:

\[
\log[Pb^{2+}] = -13.1 - \log[CO_3^{2-}]
\]

And presuming that this soluble species is the dominant one at the onset of precipitation, we set the concentration equal to the Me\(_T\) = 10\(^{-4}\)M:

\[
-4 = -13.1 - \log[CO_3^{2-}]
\]

\[
-4 = -13.1 - \log[C_T] - \log \alpha
\]

\[
\log[C_T] = -9.1 - \log \alpha
\]

**B3a:**

Substituting in for the simplified \(\log \alpha\) at \(pH < 6.3\)

\[
\log[C_T] = -9.1 - (-16.6 + 2pH)
\]

\[
\log[C_T] = +7.5 - 2pH, \quad @pH<6.3
\]

**B3b:**

And for \(pH=6.3-10.3\), we have:
Note that this is only valid up to pH 7.7, the limit of free lead’s predominance (A1 line)

Now we need to look at the PbOH+/PbCO₃ boundary: From the solubility calculations we had developed three line segments. We can conveniently take the equation for each, retaining the total carbonate term in its general form:

And for pH = 6.3-10.3, we have:

\[
\log[C_l] = -16.8 + \text{pH} - (-10.3 + \text{pH})
\]
\[
\log[C_T] = -6.5, \quad @pH = 7.7-9.4
\]

Note that this is only valid up to pH 9.4, the limit of lead monohydroxide’s predominance (A2 line).

At this point, we’re well into the PbO precipitation zone, so let’s look at the other side where lead carbonate may re-emerge at high pHs. This is beyond the A3 line, so we must consider the trihydroxide.

B5

Now looking at the final given equilibrium expression:

\[
\log [Pb(OH)_3] = -41.2 + 3pH - \log[CO_3^{2-}]
\]

And presuming that this soluble species is the dominant one at the onset of precipitation, we set the concentration equal to the \( M_{eq} = 10^{-4} \) M:

\[
-4 = -41.2 + 3pH - \log[CO_3^{2-}]
\]

\[
-4 = -41.2 + 3pH - \log[C_T] - \log\alpha
\]

\[
\log[C_T] = -37.2 + 3pH - \log\alpha
\]

B5c:

And for \( pH > 10.3 \), we have:

\[
\log[C_T] = -37.2 + 3pH - (0)
\]

\[
\log[C_T] = -37.2 + 3pH, \quad @pH > 11.0
\]
Note that this is only valid beyond pH 11, the lower limit of lead trihydroxide’s predominance (A3 line)

Type C lines
Finally, let’s consider the boundary between the two solid phases. This line will start on the low pH side, were the B lines intersect (pH=9). This is well within the zone where bicarbonate is the dominant carbonate species.

To determine this, we can pick from any one of the matched equations. Each will give us the same answer, so let’s just arbitrarily pick free lead. Now we set them equal to each other:

\[
\log[A_2] = +12.7 -2pH = \log[A_2] = -13.1 -\log[CO_3^{2-}]
\]

\[
+12.7 -2pH = -13.1 -\log[CO_3^{2-}]
\]

\[
\log[CO_3^{2-}] = -25.8 + 2pH
\]

or:

\[
\log[C_T] = -25.8 + 2pH - \log \alpha
\]

**C1b:**

And for pH=6.3-10.3, we have:

\[
\log[C_T] = -25.8 + 2pH - (-10.3 + pH)
\]

\[
\log[C_T] = -15.5 + pH, \quad @pH = 9.0-10.3
\]

**C1c:**

And for the carbonate zone; pH>10.3, we determined:

\[
\log[C_T] = -25.8 + 2pH - (0)
\]

\[
\log[C_T] = -25.8 + 2pH, \quad @pH>10.3-11.4
\]

Note that this is only valid beyond pH 11.4, the upper limit of lead oxide’s insolubility (B2 line)
And removing extra line segments and lead species that do not exist at 0.1 mM concentration (e.g., those “under” the precipitates, we get the final diagram:

\[ \text{Pb}_T = 10^{-4} \text{ M} \]
The diagram illustrates the pH vs. Log CO$_3^T$ plot for Pb$_T = 10^{-4}$ M. The following species are shown:

- Pb$^{2+}$
- PbCO$_3$(s)
- PbOH$^+$
- Pb(OH)$_3^-$
- PbO$_{(s)}$

The pH range is from 0 to 14, and Log CO$_3^T$ ranges from -14 to 0.
Some important equilibrium constants:

<table>
<thead>
<tr>
<th>Equilibria</th>
<th>Log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(OH)$_2$ (s) = Mg$^{+2}$ + 2OH$^-$</td>
<td>-11.6</td>
</tr>
<tr>
<td>Mg$^{+2}$ + H$_2$O = MgOH$^+$ + H$^+$</td>
<td>-11.44</td>
</tr>
<tr>
<td>MgCO$_3$ (s) = Mg$^{+2}$ + CO$_3^{2-}$</td>
<td>-7.5</td>
</tr>
<tr>
<td>CaCO$_3$ (s) = Ca$^{+2}$ + CO$_3^{2-}$</td>
<td>-8.34</td>
</tr>
<tr>
<td>Ca(OH)$_2$ (s) = Ca$^{+2}$ + 2OH$^-$</td>
<td>-5.19</td>
</tr>
<tr>
<td>CaSO$_4$.2H$_2$O (s) = Ca$^{+2}$ + SO$_4^{2-}$ + 2H$_2$O</td>
<td>-4.62</td>
</tr>
<tr>
<td>CaOH$^+$ = Ca$^{+2}$ + OH$^-$</td>
<td>-1.15</td>
</tr>
<tr>
<td>FeCO$_3$ (s) = Fe$^{+2}$ + CO$_3^{2-}$</td>
<td>-10.7</td>
</tr>
<tr>
<td>AlOH$^{+2}$ = Al$^{+3}$ + OH$^-$</td>
<td>-9.01</td>
</tr>
<tr>
<td>CdOH$^{+}$ = Cd$^{+2}$ + OH$^-$</td>
<td>-3.92</td>
</tr>
<tr>
<td>CoOH$^{+}$ = Co$^{+2}$ + OH$^-$</td>
<td>-4.80</td>
</tr>
<tr>
<td>CuOH$^{+}$ = Cu$^{+2}$ + OH$^-$</td>
<td>-6.00</td>
</tr>
<tr>
<td>HgOH$^{+}$ = Hg$^{+2}$ + OH$^-$</td>
<td>-10.60</td>
</tr>
<tr>
<td>NiOH$^{+}$ = Ni$^{+2}$ + OH$^-$</td>
<td>-4.14</td>
</tr>
<tr>
<td>PbOH$^{+}$ = Pb$^{+2}$ + OH$^-$</td>
<td>-6.29</td>
</tr>
<tr>
<td>ZnOH$^{+}$ = Zn$^{+2}$ + OH$^-$</td>
<td>-5.04</td>
</tr>
<tr>
<td>HgS (s) = Hg$^{+2}$ + S$^2$</td>
<td>-42.7</td>
</tr>
</tbody>
</table>

Some important half-cell reactions:

<table>
<thead>
<tr>
<th>Equ#</th>
<th>Half Cell Reaction</th>
<th>$\Delta E^\circ$ (Volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O$_2$(aq) + 4H$^+$ + 4e$^-$ = 2H$_2$O</td>
<td>+1.23</td>
</tr>
<tr>
<td>2</td>
<td>Mn$^{+3}$ + e$^-$ = Mn$^{+2}$</td>
<td>+1.51</td>
</tr>
<tr>
<td>3</td>
<td>Mn$^{+4}$ + e$^-$ = Mn$^{+3}$</td>
<td>+1.65</td>
</tr>
<tr>
<td>4</td>
<td>MnO$_4^{2-}$ + 8H$^+$ + 5e$^-$ = Mn$^{+2}$ + 4H$_2$O</td>
<td>+1.49</td>
</tr>
<tr>
<td>5</td>
<td>Fe$^{+3}$ + e$^-$ = Fe$^{+2}$</td>
<td>+0.77</td>
</tr>
<tr>
<td>6</td>
<td>Cu$^{+2}$ + e$^-$ = Cu$^+$</td>
<td>+0.16</td>
</tr>
<tr>
<td>7</td>
<td>$\frac{1}{2}$HOBBr + $\frac{1}{2}$H$^+$ + e$^-$ = $\frac{1}{2}$Br$^-$ + $\frac{1}{2}$H$_2$O</td>
<td>+1.33</td>
</tr>
<tr>
<td>8</td>
<td>O$_3$(g) + 2H$^+$ + 2 e$^-$ = O$_2$(g) + H$_2$O</td>
<td>+2.07</td>
</tr>
<tr>
<td>9</td>
<td>Al$^{+3}$ + 3e$^-$ = Al(s)</td>
<td>-1.68</td>
</tr>
<tr>
<td>10</td>
<td>$\frac{1}{2}$HOCl + $\frac{1}{2}$H$^+$ + e$^-$ = $\frac{1}{2}$Cl$^-$ + $\frac{1}{2}$H$_2$O</td>
<td>+1.48</td>
</tr>
<tr>
<td>11</td>
<td>$\frac{1}{2}$OCl$^-$ + H$^+$ + e$^-$ = $\frac{1}{2}$Cl$^-$ + $\frac{1}{2}$H$_2$O</td>
<td>+1.64</td>
</tr>
<tr>
<td>12</td>
<td>BrO$_3^-$ +5H$^+$ +4e$^-$ = HOBBr + 2H$_2$O</td>
<td>+1.45</td>
</tr>
<tr>
<td>13</td>
<td>$\frac{1}{2}$NH$_2$Cl + H$^+$ + e$^-$ = $\frac{1}{2}$Cl$^-$ + $\frac{1}{2}$NH$_4^+$</td>
<td>+1.40</td>
</tr>
<tr>
<td>14</td>
<td>Fe(OH)$_3$(am) + 3H$^+$ + e$^-$ = Fe$^{+2}$ + 3H$_2$O</td>
<td>+0.95</td>
</tr>
<tr>
<td>15</td>
<td>SO$_4^{2-}$ + 9H$^+$ + 8e$^-$ = HS + 4H$_2$O</td>
<td>+0.25</td>
</tr>
<tr>
<td>16</td>
<td>S(s) + 2H$^+$ + 2e$^-$ = H$_2$S(g)</td>
<td>+0.17</td>
</tr>
<tr>
<td>17</td>
<td>Zn$^{+2}$ + 2e$^-$ = Zn(s)</td>
<td>-0.76</td>
</tr>
<tr>
<td>18</td>
<td>Ni$^{+2}$ + 2e$^-$ = Ni(s)</td>
<td>-0.24</td>
</tr>
<tr>
<td>19</td>
<td>Pb$^{+2}$ + 2e$^-$ = Pb(s)</td>
<td>-0.126</td>
</tr>
<tr>
<td>20</td>
<td>ClO$_2$ + e$^-$ = ClO$_2^-$</td>
<td>+0.95</td>
</tr>
<tr>
<td>21</td>
<td>PbO$_2$(s) + 4H$^+$ + 2e$^-$ = Pb$^{+2}$ + 2H$_2$O</td>
<td>+1.451</td>
</tr>
</tbody>
</table>
### Properties of Selected Elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Atomic #</th>
<th>Atomic Wt.</th>
<th>Valence</th>
<th>Electronegativity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>Al</td>
<td>13</td>
<td>26.98</td>
<td>3</td>
<td>1.47</td>
</tr>
<tr>
<td>Bromine</td>
<td>Br</td>
<td>35</td>
<td>79.904</td>
<td>1,3,5,7</td>
<td>2.74</td>
</tr>
<tr>
<td>Calcium</td>
<td>Ca</td>
<td>20</td>
<td>40.08</td>
<td>2</td>
<td>1.04</td>
</tr>
<tr>
<td>Carbon</td>
<td>C</td>
<td>6</td>
<td>12.01</td>
<td>2,4</td>
<td>2.50</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Cl</td>
<td>17</td>
<td>35.453</td>
<td>1,3,5,7</td>
<td>2.83</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu</td>
<td>29</td>
<td>63.54</td>
<td>1,2</td>
<td>1.75</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H</td>
<td>1</td>
<td>1.01</td>
<td>1</td>
<td>2.20</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe</td>
<td>26</td>
<td>55.845</td>
<td>0,2,3</td>
<td>1.83</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg</td>
<td>12</td>
<td>24.31</td>
<td>2</td>
<td>1.23</td>
</tr>
<tr>
<td>Manganese</td>
<td>Mn</td>
<td>25</td>
<td>54.94</td>
<td>2</td>
<td>1.60</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N</td>
<td>7</td>
<td>14.0047</td>
<td>3,5</td>
<td>3.07</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O</td>
<td>8</td>
<td>16.00</td>
<td>2</td>
<td>3.50</td>
</tr>
<tr>
<td>Potassium</td>
<td>K</td>
<td>19</td>
<td>39.10</td>
<td>1</td>
<td>0.91</td>
</tr>
<tr>
<td>Sodium</td>
<td>Na</td>
<td>11</td>
<td>22.99</td>
<td>1</td>
<td>1.01</td>
</tr>
<tr>
<td>Strontium</td>
<td>Sr</td>
<td>38</td>
<td>87.62</td>
<td>2</td>
<td>0.99</td>
</tr>
<tr>
<td>Sulfur</td>
<td>S</td>
<td>16</td>
<td>32.06</td>
<td>2,4,6</td>
<td>2.44</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn</td>
<td>30</td>
<td>65.39</td>
<td>2</td>
<td>1.65</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb</td>
<td>82</td>
<td>207.19</td>
<td>2,4</td>
<td></td>
</tr>
</tbody>
</table>

### Selected Acidity Constants

(Aqueous Solution, 25°C, I = 0)

<table>
<thead>
<tr>
<th>NAME</th>
<th>FORMULA</th>
<th>pKₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perchloric acid</td>
<td>HClO₄ = H⁺ + ClO₄⁻</td>
<td>-7</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>HCl = H⁺ + Cl⁻</td>
<td>-3</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>H₂SO₄ = H⁺ + HSO₄⁻</td>
<td>-3</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>HNO₃ = H⁺ + NO₃⁻</td>
<td>0</td>
</tr>
<tr>
<td>Bisulfate ion</td>
<td>HSO₄⁻ = H⁺ + SO₄²⁻</td>
<td>2</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>H₃PO₄ = H⁺ + H₂PO₄⁻</td>
<td>2.15</td>
</tr>
<tr>
<td>o-Phthalic acid</td>
<td>C₆H₄(COOH)₂ = H⁺ + C₆H₄(COOH)COO⁻</td>
<td>2.89</td>
</tr>
<tr>
<td>p-Hydroxybenzoic acid</td>
<td>C₆H₄(OH)COOH = H⁺ + C₆H₄(OH)COO⁻</td>
<td>4.48</td>
</tr>
<tr>
<td>Nitrous acid</td>
<td>HNO₂ = H⁺ + NO₂⁻</td>
<td>4.5</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>CH₃COOH = H⁺ + CH₃COO⁻</td>
<td>4.75</td>
</tr>
<tr>
<td>Aluminum ion</td>
<td>Al(H₂O)₆⁺³ = H⁺ + Al(OH)(H₂O)₅⁺²</td>
<td>4.8</td>
</tr>
<tr>
<td>Carbonic acid</td>
<td>H₂CO₃ = H⁺ + HCO₃⁻</td>
<td>6.35</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>H₂S = H⁺ + HS⁻</td>
<td>7.02</td>
</tr>
<tr>
<td>Dihydrogen phosphate</td>
<td>H₂PO₄⁻ = H⁺ + HPO₄⁻²</td>
<td>7.2</td>
</tr>
</tbody>
</table>
Hypochlorous acid \[ \text{HOCl} = \text{H}^+ + \text{OCl}^- \] 7.5

Hypobromous acid \[ \text{HOBr} = \text{H}^+ + \text{OBr}^- \] 8.71

Ammonium ion \[ \text{NH}_4^+ = \text{H}^+ + \text{NH}_3 \] 9.24

Bicarbonate ion \[ \text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-} \] 10.33

Monohydrogen phosphate \[ \text{HPO}_4^{2-} = \text{H}^+ + \text{PO}_4^{3-} \] 12.3

Sulfide \[ \text{HS}^- = \text{H}^+ + \text{S}^{2-} \] 13.9

### Atmospheric Gases

<table>
<thead>
<tr>
<th>Gas</th>
<th>Atmospheric Abundance</th>
<th>Henry's Law Const$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nitrogen</strong> (N$_2$)</td>
<td>780,840 ppmv (78.084%)</td>
<td>6.1 x 10$^{-4}$</td>
</tr>
<tr>
<td><strong>Oxygen</strong> (O$_2$)</td>
<td>209,460 ppmv (20.946%)</td>
<td>1.3 x 10$^{-3}$</td>
</tr>
<tr>
<td><strong>Argon</strong> (Ar)</td>
<td>9,340 ppmv (0.9340%)</td>
<td>1.4 x 10$^{-3}$</td>
</tr>
<tr>
<td><strong>Carbon dioxide</strong> (CO$_2$)</td>
<td>387 ppmv (0.0387%)</td>
<td>3.4 x 10$^{-2}$</td>
</tr>
<tr>
<td><strong>Neon</strong> (Ne)</td>
<td>18.18 ppmv (0.001818%)</td>
<td>4.5 x 10$^{-4}$</td>
</tr>
<tr>
<td><strong>Helium</strong> (He)</td>
<td>5.24 ppmv (0.000524%)</td>
<td>3.7 x 10$^{-4}$</td>
</tr>
<tr>
<td><strong>Methane</strong> (CH$_4$)</td>
<td>1.79 ppmv (0.000179%)</td>
<td></td>
</tr>
<tr>
<td><strong>Krypton</strong> (Kr)</td>
<td>1.14 ppmv (0.000114%)</td>
<td></td>
</tr>
<tr>
<td><strong>Hydrogen</strong> (H$_2$)</td>
<td>0.55 ppmv (0.000055%)</td>
<td>7.8 x 10$^{-4}$</td>
</tr>
<tr>
<td><strong>Nitrous oxide</strong> (N$_2$O)</td>
<td>0.3 ppmv (0.00003%)</td>
<td></td>
</tr>
<tr>
<td><strong>Xenon</strong> (Xe)</td>
<td>0.09 ppmv (9x10$^{-6}$%)</td>
<td></td>
</tr>
</tbody>
</table>

$\alpha_2$ for a diprotic acid:

$$\alpha_2 = \frac{1}{K_1K_2 + \frac{[H^+]^2}{K_2} + 1}$$

$^3$ In: moles/L/atm