Problem #1 (2 points)
1. Determine the pH and alkalinity for the following solutions. Assume the systems are closed to the atmosphere.
   a. 5x10^{-4}F NaOH
   b. 5x10^{-5}F Na_{2}CO_{3}
   c. 5x10^{-5}F KHCO_{3}
   d. 1x10^{-3}F HCl

Solution to #1

Please note that alkalinity in these problems can be most easily determined by the sum of the base cations minus the acid anions (Alk = C_B - C_A).

a. 5x10^{-4}F NaOH
This is a strong base,
\[ [\text{OH}^-] = [\text{Na}^+] = 5 \times 10^{-4} \]

<table>
<thead>
<tr>
<th>pH</th>
<th>Alk</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.7</td>
<td>5 \times 10^{-4} \text{ eq/L} = 25 \text{ mg/L as CaCO}_3</td>
</tr>
</tbody>
</table>

b. 5x10^{-5}F Na_{2}CO_{3}
This is a weak base. The problem can be solved with a log C vs pH diagram and the following proton balance equation:
\[ 2[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{H}^+] = [\text{OH}^-] \]
which reduces to:
\[ [\text{HCO}_3^-] = [\text{OH}^-] \]

<table>
<thead>
<tr>
<th>pH</th>
<th>Alk</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.7</td>
<td>10^{-4} \text{ eq/L} = 5 \text{ mg/L as CaCO}_3</td>
</tr>
</tbody>
</table>
c. $5 \times 10^{-5} F \text{ KHCO}_3$
This is a weak base. The problem can be solved with a log C vs pH diagram and the following
proton balance equation:

$$[\text{H}_2\text{CO}_3] + [\text{H}^+] = [\text{OH}^-] + [\text{CO}_3^{2-}]$$

which reduces to:

$$[\text{H}_2\text{CO}_3] = [\text{OH}^-]$$

<table>
<thead>
<tr>
<th>pH = 8.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alk = $5 \times 10^{-5}$ eq/L = 2.5 mg/L as CaCO$_3$</td>
</tr>
</tbody>
</table>

d. $1 \times 10^{-3} F \text{ HCl}$
This is a strong acid,

$$[\text{Cl}^-] = [\text{H}^+] = 1 \times 10^{-3}$$

<table>
<thead>
<tr>
<th>pH = 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alk = $-1 \times 10^{-3}$ eq/L = -50 mg/L as CaCO$_3$</td>
</tr>
</tbody>
</table>

Problem #2 (1 point)
2. What partial pressure of carbon dioxide are the solutions from question #1 in equilibrium with?

Solution to #2
Please note that while closed systems may not have any open air/water interface, there is still a
calculated value for the partial pressure of CO$_2$ that the solution is in equilibrium with, and that
value is often non-zero. Also note that many closed systems do have air/water interfaces, but
they may be considered closed because either (1) the interface has not existed long enough to
allow for equilibrium to have occurred, or (2) the volume of the air space is too small to affect
the CO$_2$ concentration in the water.

$$[H_2CO_3^+] = k_H p_{CO_2}$$

$$[H_2CO_3^+] = \alpha_q C_T$$

$$p_{CO_2} = \frac{C_T \alpha_q}{k_H}$$

a. $5 \times 10^{-4} F \text{ NaOH}$
$C_T = 0$, so:

$$p_{CO_2} = 0$$
b. $5 \times 10^{-5}F \text{ Na}_2\text{CO}_3$

$C_T = 5 \times 10^{-5}$, and pH = 9.7, so:
$\alpha_0 \sim \frac{[H^+]}{k_1} = \frac{10^{-9.7}}{10^{-6.3}} = 10^{-3.4}$
$p_{\text{CO}_2} = 5 \times 10^{-5} \frac{10^{-3.4}}{10^{-1.5}}$

$p_{\text{CO}_2} = 6.3 \times 10^{-7} = 10^{-6.2}$

You can also do this by using the $[\text{H}_2\text{CO}_3]$ determined for problem 1b, but note that this value is really $[\text{H}_2\text{CO}_3^+]$ which is about equal to the aqueous carbon dioxide concentration $[\text{CO}_2 \text{ (aq)}]$. Therefore, there is no need to multiply by 630 (i.e., the ratio of $[\text{CO}_2 \text{ (aq)}]/[\text{H}_2\text{CO}_3]$).

c. $5 \times 10^{-5}F \text{ KHCO}_3$

$C_T = 5 \times 10^{-5}$, and pH = 8.0, so:
$\alpha_0 \sim \frac{[H^+]}{k_1} = \frac{10^{-8.0}}{10^{-6.3}} = 10^{-1.7}$
$p_{\text{CO}_2} = 5 \times 10^{-5} \frac{10^{-1.7}}{10^{-1.5}}$

$p_{\text{CO}_2} = 3.2 \times 10^{-5} = 10^{-4.5}$

d. $1 \times 10^{-3}F \text{ HCl}$

$C_T = 0$, so:

$p_{\text{CO}_2} = 0$

Problem #3

3. Repeat question #1, but assume the systems are open to the atmosphere.

Solution to #3 (1 point)

Draw an open system, log C vs pH diagram, and solve using the electroneutrality equation.

a. $5 \times 10^{-4}F \text{ NaOH}$

ENE:

$[\text{Na}^+] + [\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$

which reduces to:

$[\text{Na}^+] = [\text{HCO}_3^-]$

$pH = 8.0$

$\text{Alk} = 5 \times 10^{-4} \text{ eq/L} = 25 \text{ mg/L as CaCO}_3$
**b. 5x10^{-5}F Na_2CO_3**

ENE:

\[
[Na^+] + [H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]
\]

which reduces to:

\[
[Na^+] = [HCO_3^-]
\]

<table>
<thead>
<tr>
<th>( pH )</th>
<th>Alk</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.3</td>
<td>1 x 10^{-4} eq/L = 5 mg/L as CaCO_3</td>
</tr>
</tbody>
</table>

**c. 5x10^{-5}F KHCO_3**

ENE:

\[
[K^+] + [H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]
\]

which reduces to:

\[
[K^+] = [HCO_3^-]
\]

<table>
<thead>
<tr>
<th>( pH )</th>
<th>Alk</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.0</td>
<td>5 x 10^{-5} eq/L = 2.5 mg/L as CaCO_3</td>
</tr>
</tbody>
</table>

**d. 1x10^{-3}F HCl**

ENE:

\[
[H^+] = [OH^-] + [Cl^-] + [HCO_3^-] + 2[CO_3^{2-}]
\]

which reduces to:

\[
[H^+] = [Cl^-]
\]

<table>
<thead>
<tr>
<th>( pH )</th>
<th>Alk</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>-1 x 10^{-3} eq/L = -50 mg/L as CaCO_3</td>
</tr>
</tbody>
</table>

**Problem #4 (1 point)**

4. A groundwater was found to have the following composition:

ANC = 3x10^{-2} equ/L, \( pH = 7.5 \)

What is the partial pressure of CO_2 that is in equilibrium with this water?

**Solution to #4**

Assume all ANC is due to carbonate species; which at pH 7.5 is almost entirely bicarbonate. Therefore:

\[
[HCO_3^-] = 3 \times 10^{-2}
\]

and since

\[
[H_2CO_3] = [HCO_3^-][H^+]/k_1
\]
so:

\[ [\text{H}_2\text{CO}_3^+] = (3 \times 10^{-2})(10^{-7.5})/10^{-6.3} \]

\[ [\text{H}_2\text{CO}_3^+] = 10^{-2.7} \]

now:

\[ [\text{H}_2\text{CO}_3^+] = k_H \times p_{\text{CO}_2} \]

\[ p_{\text{CO}_2} = 10^{-2.7}/10^{-1.5} = 10^{-1.2} = 0.063 \text{ atm} \]

**Problem #5 (1 point)**

5. A surface water and a groundwater are to be used as a raw water supply for the town of Springfield, FL. They will be mixed as follows:

<table>
<thead>
<tr>
<th></th>
<th>Surface Water</th>
<th>Groundwater</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow Rate</td>
<td>3.5 MGD</td>
<td>0.8 MGD</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>10 mg/L as CaCO\textsubscript{3}</td>
<td>250 mg/L as CaCO\textsubscript{3}</td>
</tr>
<tr>
<td>pH</td>
<td>6.9</td>
<td>8.3</td>
</tr>
</tbody>
</table>

What will the pH of the combined waters be?

**Solution to #5**

Recognize that this must be a closed system. The mixing of waters within an engineered treatment system that does not specifically include aeration or multi-day open-air storage will not result in substantial transfer of CO\textsubscript{2} across the air water interface.

Also recognize that a high level of precision (i.e., significant figures) is needed for the intermediate calculations in order to have an accurate value for the difference between the total carbonates (C\textsubscript{T}) and the alkalinity (Alk). This is key to getting an accurate value for the blended pH.

The final pH should be somewhere between the pHs of the two waters being blended. If you get a pH outside of this range, you should be suspicious that a mistake was made. You can also use a nomograph to check very roughly on your result. However, don’t rely on nomographs for accurate determination of blended water pH. They usually cannot be read with an adequate degree of accuracy.

**First Calculate C\textsubscript{T} for both waters:**

\[ C_T = \frac{Alk - [OH^-] + [H^+]}{\alpha_1 + 2\alpha_2} \]

Surface Water:  
\[ C_T = ((10/50,000) - 10^{-7.1} + 10^{-6.9})/0.78048 = 2.563 \times 10^{-4} \text{ M} = 10^{-3.59} \]

Groundwater:  
\[ C_T = ((250/50,000) - 10^{-5.7} + 10^{-8.3})/0.99815 = 5.007 \times 10^{-3} \text{ M} = 10^{-2.30} \]

**Next Determine the Blended C\textsubscript{T} and Alk**

\[ C_{T(\text{blend})} = (3.5(2.563 \times 10^{-4}) + 0.8(5.007 \times 10^{-3}))/3.5 + 0.8) = 1.140 \times 10^{-3} \text{ M} \]

\[ \text{Alk}_{(\text{blend})} = (3.5(10/50,000) + 0.8(250/50,000))/(3.5 + 0.8) = 1.093 \times 10^{-3} \text{ eq/L} \]
Lastly, Determine pH of the Blended Water

Since the pH of both waters is well below the pk₂, carbonate is likely to be insignificant as compared to bicarbonate. This means that the alkalinity is composed almost entirely of bicarbonate, so:

\[
\text{Alk} \approx \alpha_1 C_T \\
\approx \left( \frac{1}{\left[ H^+ \right]} + 1 + \frac{k_2}{k_1} \right) \frac{C_T}{\left[ H^+ \right]} \quad \left( \begin{array}{c} \approx \frac{C_T}{\left[ H^+ \right]} + 1 \end{array} \right)
\]

now insert Alk and C_T and solve for H⁺, and we get:

\[
[H^+] = 1.87 \times 10^{-8}
\]

\[\text{pH} = 7.73\]

Solution to #6 (1 Point)

Problem statement:
A railroad car spills its cargo of phenol into a drinking water reservoir. The plume quickly reaches the water treatment plant intake. The mayor and water superintendent want you to tell them how much of the phenol will be removed by the treatment system before the water gets to the first consumer. The plant uses conventional treatment (coagulation, settling, anthracite/sand filtration followed by final free chlorination). Your research tells you that the only process in this treatment system that will result in removal/destruction of phenol is the free chlorination. The plant uses a dose which gives them a residual of 1 mg/L. The first consumer gets water that has had a chlorine contact time of 2 hrs.

Your literature search leads you to the kinetic study by Deborde & von Gunten, 2008 [Wat. Res. 42(1)13] which describes the rate of phenol destruction as first order in HOCl and first order in the phenate anion.

\[
\frac{d[\text{phenol}_{\text{total}}]}{dt} = -k[\text{phenate}][\text{HOCl}] = -k_{\text{cond}}[\text{phenol}_{\text{total}}][\text{TRC}]
\]

You know from Deborde & von Gunten that the value for k is \(2.19 \times 10^{-4}\) M⁻¹s⁻¹. And from basic kinetic theory, you know that this will be a pseudo-1ˢ order reaction, and thus:

\[
\text{fraction remaining}_{t=\text{time}} = \frac{[\text{phenol}_{\text{total}}]_{\text{time}}}{[\text{phenol}_{\text{total}}]_{\text{time}=0}} = e^{-k_{\text{cond}}[\text{TRC}]t}
\]
a. Develop an equation that gives you the “conditional” $k$ ($k_{\text{cond}}$) for this reaction as a function of $[H^+]$.

b. Graph the fraction remaining vs pH over the entire range (0-14). Don’t be stingy with the points to be plotted (graph at least one point for every 0.1 pH units). Since this is a model, show only lines not data symbols.

c. Graph the log removal of total phenol vs pH over the same range.

d. If the treatment system normally distributes water at pH 7.0, how would you recommend they change their pH control practice during the time of the phenol spill?

---

**Equation for conditional $K$**

\[
\frac{d[\text{phenol}_{\text{total}}]}{dt} = -k[\text{phenate}][\text{HOCl}] = -k_{\text{cond}}[\text{phenol}_{\text{total}}][\text{TRC}]
\]

\[
k[\text{phenate}][\text{HOCl}] = k_{\text{cond}}[\text{phenol}_{\text{total}}][\text{TRC}]
\]

\[
k_{\text{cond}} = k \frac{[\text{phenate}]}{[\text{phenol}_{\text{total}}]} \frac{[\text{HOCl}]}{[\text{TRC}]}
\]

\[
k_{\text{cond}} = k \alpha_1 \text{phenol} \alpha_0 \text{chlorine}
\]

Where for a monoprotic acid (both HOCl and Phenol are monoprotic acids):

\[
\alpha_0 = \frac{1}{K_a \frac{[H^+]}{} + 1}
\]

\[
\alpha_1 = \frac{1}{1 + \frac{[H^+]}{K_a}}
\]

And the $K_a$ values are $10^{-7.5}$ for HOCl/OCl- and $10^{-9.9}$ for phenol/phenate, and $k = 2.19 \times 10^4$ M$^{-1}$s$^{-1}$

So:

\[
k_{\text{cond}} = 2.19 \times 10^4 \left( \frac{1}{1 + \frac{[H^+]}{10^{-9.5}}} \right) \left( \frac{1}{\frac{10^{-7.5}}{[H^+]} + 1} \right) \text{M}^{-1}\text{s}^{-1}
\]
Also note that FRC (HOCl and OCl⁻) are expressed as mg/L as Cl₂, so the GFW is 71 g/mole, not 51.5 or 52.5 g/mole.

**Graph of fraction remaining**

\[
\log f_{\text{remaining}} = \log \left( \frac{f_{\text{remaining}}}{f_{\text{initial}}} \right) = e^{-k_{\text{cond}}[\text{TRC}]t}
\]

**Graph of log removal**

Note that “log removal” is a common term used by environmental engineers to mean the negative log of the fraction remaining. Therefore, if you have 10% remaining (fraction remaining is 0.1), you have 1 log removal. If you have 1% remaining (fraction remaining is 0.01), you have 2 log removal, and so on. It is **not** the log of the % removal, nor the log fraction removed.

\[
\log \text{removal} \equiv \log(fraction \text{ removal}_t) = \log(e^{-k_{\text{cond}}[\text{TRC}]t}) = \log e^{-k_{\text{cond}}[\text{TRC}]t}
\]
**Recommended pH change**

Best to raise the pH up to as close to 8.7 as practical.
Summary:

Prob 1

<table>
<thead>
<tr>
<th>pH</th>
<th>Alkalinity (mg/L)</th>
<th>(equ/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>10.7</td>
<td>25</td>
</tr>
<tr>
<td>b</td>
<td>9.7</td>
<td>5</td>
</tr>
<tr>
<td>c</td>
<td>8.0</td>
<td>2.5</td>
</tr>
<tr>
<td>d</td>
<td>3.0</td>
<td>-50</td>
</tr>
</tbody>
</table>

Prob 2

<table>
<thead>
<tr>
<th>Pco2</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
</tr>
<tr>
<td>b</td>
</tr>
<tr>
<td>c</td>
</tr>
<tr>
<td>d</td>
</tr>
</tbody>
</table>

Prob 3

<table>
<thead>
<tr>
<th>pH</th>
<th>Alkalinity (mg/L)</th>
<th>(equ/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>8.0</td>
<td>25</td>
</tr>
<tr>
<td>b</td>
<td>7.3</td>
<td>5</td>
</tr>
<tr>
<td>c</td>
<td>7.0</td>
<td>2.5</td>
</tr>
<tr>
<td>d</td>
<td>3.0</td>
<td>-50</td>
</tr>
</tbody>
</table>

Prob 4

<table>
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<tr>
<th>Pco2</th>
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</thead>
<tbody>
<tr>
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</table>

Prob 5

<table>
<thead>
<tr>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.73</td>
</tr>
</tbody>
</table>

Prob 6

\[ k_{\text{cond}} = 2.19 \times 10^{+4} \left( \frac{1}{1 + \frac{10^{-8.5}}{[H^+]}} \right) \left( \frac{1}{\frac{10^{-7.5}}{[H^+]} + 1} \right) M^{-1} s^{-1} \]

graphs