Acid-base systems I
Weak acids & bases

- Many of the important properties of natural waters and wastewaters are due to the presence of weak acid, weak bases, and their salts
  - Carbonate species ($\text{HCO}_3^-$ & $\text{CO}_3^{2-}$) in natural waters and their buffering effect
  - Ammonia speciation ($\text{NH}_3$ & $\text{NH}_4^+$) in water
  - Speciation of hypochlorous acid ($\text{HOCl}$ & $\text{OCl}^-$) in chlorine disinfection

- Monoprotic vs. polyprotic acids
  - Monoprotic: contains only one exchangeable $\text{H}^+$ ion
    ex: HCl, HOCl, CH$_3$COOH
  - Polyprotic: contains two or more exchangeable $\text{H}^+$ ions
    ex: H$_2$SO$_4$, H$_2$CO$_3$, H$_3$PO$_4$
Analyzing monoprotic weak acid/base system

- $10^{-3}$ M CH₃COOH (HAc) is added in pure water at 25°C. What will be the pH of the water? What will be the HAc and Ac⁻ concentrations?

Reaction: \[ \text{HAc} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{Ac}^- \]

$C_T = 10^{-3}$ M, $pK_a = 4.75$ (at 25°C)

Species involved (4):
- $H^+$ ($\text{H}_3\text{O}^+$), $\text{OH}^-$, HAc, Ac⁻

→ Need 4 equations!
Analyzing monoprotic weak acid/base system

Equilibrium constants:

Mass balance:

Charge balance (electroneutrality):
Analyzing monoprotic weak acid/base system

Assuming $[H^+] >> [OH^-]$ (acidic), we can solve the equation to get

$$[H^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_aC_T}}{2}$$

As $K_a = 10^{-4.75}$ & $K_w = 10^{-14}$ at 25°C,

$$[H^+] = 1.25 \times 10^{-4} \text{ M} \quad \text{(pH}=3.9)$$

$$[OH^-] = 8.00 \times 10^{-11} \text{ M} \quad \text{(assumption holds)}$$

$$[Ac^-] = 1.25 \times 10^{-4} \text{ M} \quad \text{(A weak acid} \rightarrow \text{ partial dissociation)}$$

$$[HAc] = 8.75 \times 10^{-4} \text{ M}$$
Analyzing monoprotic weak acid/base system

The question can be solved using \([H^+]\) as a major variable:

\[
(2) + (3): \quad [Ac^-] = \frac{C_T K_a}{K_a + [H^+]} \quad (5)
\]

\[
(3) + (5): \quad [HAc] = \frac{C_T [H^+]}{K_a + [H^+]} \quad (6)
\]

\[
(1): \quad [OH^-] = \frac{K_w}{[H^+]} \quad (7)
\]
Analyzing monoprotic weak acid/base system
Actually drawing the pH-pC diagram for a monoprotic acid is quite simple!
Analyzing monoprotic weak acid/base system

For different $C_T$ (acetic acid, $pK_a=4.75$):
Analyzing monoprotic weak acid/base system

For different $K_a$ ($C_T=10^{-3} \text{ M}$):

- Formic acid, $pK_a=3.75$
- Acetic acid, $pK_a=4.75$
- Hypochlorous acid, $pK_a=7.53$
Analyzing monoprotic weak acid/base system

Q: What if there are multiple acids in water?

ex) 

<table>
<thead>
<tr>
<th>Acids</th>
<th>( C_T ) (M)</th>
<th>( pK_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAc</td>
<td>( 10^{-6} )</td>
<td>4.75</td>
</tr>
<tr>
<td>HOCl</td>
<td>( 10^{-3} )</td>
<td>7.53</td>
</tr>
<tr>
<td>HCN</td>
<td>( 10^{-4} )</td>
<td>9.40</td>
</tr>
</tbody>
</table>
Analyzing monoprotic weak acid/base system
**Dominant vs. Trace acid/base systems**

So:

- Usually one or two acid/base systems dominate a system, setting the pH value
- All other trace acid/base systems will adjust to the pH value
  (dissociated according to the pH value set by the dominant acid/base systems)
Analyzing monoprotic weak acid/base system

What about a “salt” of a “conjugate base” of a weak acid?

\[
\text{HAc} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{Ac}^-
\]

Acid \quad \text{Base} \quad \text{Conjugate acid} \quad \text{Conjugate base}

• Brønsted-Lowry acid & base
  – Brønsted-Lowry acid: any substance that can donates a proton (i.e., proton donor)
  – Brønsted-Lowry base: any substance that can accepts a proton (i.e., proton acceptor)
Analyzing monoprotic weak acid/base system

NaAc as an example:

Equilibrium constants

\[ K_w = [H^+][OH^-] \]

\[ K_a = \frac{[H^+][Ac^-]}{[HAc]} \]

Mass balance

Charge balance
Analyzing monoprotic weak acid/base system

\[ \text{CT} = 10^{-3} \text{ M} \]
\[ \text{pK}_a = 4.75 \]
**pH buffer**

Weak acid + salt of its conjugate base
Homework:
5x10^{-4} M NaAc and 5x10^{-4} M HAc is added in pure water to make a buffer solution with C_T=10^{-3} M. **What is the pH of the buffer?**