COMMON ION & BUFFER PROBLEMS

General comments:

- Omit neutral spectator ions for salt solutions, use the acidic or basic ion in your reactions. e.g. for NaF, Na\(^+\) is neutral spectator, F\(^-\) is weak base.

- If you have mixture of WA (HA) and salt containing conj base (A\(^-\)), write the WA hydrolysis reaction. You have a mixture of reactants (HA) and products (A\(^-\)). HA and A\(^-\) don’t react! (Similarly, if you have a mixture of a WB and its conj acid, write the WB hydrolysis reaction.)

- For SA’s, \([HA] = [H_3O^+]\). For group IA SB’s, \([SB] = [OH^-]\)

- If volume is not given or if only one volume is given, you can assume the volume stayed constant and you may use initial M's in HH or K\(_a\) expression. If different volumes are given when the solutions are mixed, you must calculate the moles (or diluted M's) before plugging them into ICE or ICF table, or HH equation. (see problem 2 b for example.)

- Only use HH equation if you have a conjugate acid-base pair (HA & A\(^-\)) present initially. Do not use HH if your primary substance is one of the following: SA, SB, WA or WB. The only time you may use HH equation for titration problems is for the buffer region (before eq pt) of a WA/SB titration.

- For ICE tables in WA, WB and buffer problems we assume H\(_3\)O\(^+\) (or OH\(^-\) for WB) is initially 0 M even though there is a tiny amount present from autoionization of water (and other hydrolysis processes.)

1) a) What is the pH of a 1.00 M HF solution? K\(_a\) = 7.0\(\times\)10\(^{-4}\) HF is WA-should recognize this from its formula and its K\(_a\) value!

Strategy: Write WA equilibrium reaction, Set up ICE & K\(_a\), x = [H\(_3\)O\(^+\)]

**WA hydrolysis:** HF\((aq)\) + H\(_2\)O\((l)\) ⇌ H\(_3\)O\(^+\)(aq) + F\(^-(aq)\)

<table>
<thead>
<tr>
<th></th>
<th>HF((aq)) + H(_2)O((l)) ⇌ H(_3)O(^+)(aq) + F(^-(aq))</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>[HF]</td>
</tr>
<tr>
<td>C</td>
<td>-x</td>
</tr>
<tr>
<td>E</td>
<td>1.00 - x</td>
</tr>
</tbody>
</table>

\[K_a = \frac{[H_3O^+][F^-]}{[HF]}\] Assume x is much smaller than initial [ HA]

\[x^2 = 1.00(7.0 \times 10^{-4}) = 7.0 \times 10^{-4}\]
\[x = \sqrt{7.0 \times 10^{-4}} = 0.0265\]
\[x = [H_3O^+] = 0.0265 \text{ M}\]

- **check assumption:** \[\frac{x}{[HA]_{initial}} \times 100 = \frac{0.0265}{1.00} \times 100 = 2.65 \% < 5\% \checkmark\]

\[pH = -\log [H_3O^+]\]
\[pH = -\log 0.0265\]
\[pH = 1.58\] (or pH = 1.59 if used \([H_3O^+] = .026)\]

b) What is the pH of 1.00 M HF solution after adding 0.500 M NaF? For HF, K\(_a\) = 7.0\(\times\)10\(^{-4}\)

NaF is a soluble salt in aq. solutions: NaF\((aq)\) → Na\(^+\) + F\(^-\)

N B F\(^-\) is conj base of HF

\[|F\rangle = |NaF\rangle = 0.500 \text{ M (because it's a 1:1 ratio)}\]

Have mixture of WA (HF) and conj base (F). F\(^-\) is a common ion for WA eq rxn.

**Strategy:** Write WA eq rxn, Plug both [HF] and [F] into ICE and K\(_a\), x = [H\(_3\)O\(^+\)].

- HH may be used to solve this since we have combination of WA & conj base!
WA hydrolysis: \( \text{HF}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{F}^-(aq) \)

- V not given so assume V is constant, plug initial M's into table.
- \([\text{H}_3\text{O}^+] = 0\) M initially; we are assuming that HA and \(\text{A}^-\) are added at the same time and we ignore the small amount of \(\text{H}_3\text{O}^+\) formed from the autoionization of water. Thus \(x = [\text{H}_3\text{O}^+]\) = amount of acid ionized in the presence of the common ion.

<table>
<thead>
<tr>
<th></th>
<th>(\text{HF}(aq))</th>
<th>(\text{H}_2\text{O}(l))</th>
<th>(\text{H}_3\text{O}^+(aq))</th>
<th>(\text{F}^-(aq))</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.00</td>
<td>0</td>
<td>0.500</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>1.00-x</td>
<td>x</td>
<td>0.500+x</td>
<td></td>
</tr>
</tbody>
</table>

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} \quad \text{Assume } x \text{ is much smaller than initial } [\ ]'s: \quad 7.0 \times 10^{-4} = \frac{x(0.500)}{1.00} \\
x = \frac{1.00(7.0 \times 10^{-4})}{0.500} = 1.4 \times 10^{-3} \quad x = [\text{H}_3\text{O}^+] = 1.4 \times 10^{-3} \text{ M} \\
pH = -\log[\text{H}_3\text{O}^+] \quad \text{pH} = -\log 1.4 \times 10^{-3} \quad \text{pH} = 2.85
\]

\(\text{pH} \uparrow\) when NaF, a basic salt, was added. Adding \(\text{F}^-, \) a common ion, causes \([\text{H}_3\text{O}^+]\downarrow.\) Adding a common ion suppresses the dissociation of a WA (HF) so less \(\text{H}_3\text{O}^+\) is formed.

*Note: may use HH to calc pH instead of finding \(x\) from \(K_a\): see following problem.

2) a) What is the pH of 500.0 mL of 0.10 M formic acid (\(\text{HCO}_2\)H) combined with 400.0 mL of 0.20 M sodium formate (NaHCO\(_2\))? \(K_a = 1.8 \times 10^{-4}\)

NaHCO\(_2\) is a soluble salt: \(\text{NaHCO}_2 \rightarrow \text{Na}^+ + \text{HCO}_2^-\)

Initial M’s: \([\text{HCO}_2^-] = [\text{NaHCO}_2] = 0.20 \text{ M } \text{HCO}_2^-\) \([\text{HCO}_2\text{H}] = 0.10 \text{ M } \text{HCO}_2\text{H}\)

Have mixture of WA (HCO\(_2\)H) and conj. base (HCO\(_2^-\)). This is buffer mixture!

Strategy: Write WA eq rxn, use HH equation to find pH. Alternately you may set up ICE & \(K_a\) to find \(x = [\text{H}_3\text{O}^+]\) (See problem 1b above)

WA hydrolysis: \(\text{HCO}_2\text{H}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HCO}_2^- (aq)\)

Note: Don't use the original M's in the ICE/ICF table, \(K_a\) expression, or the HH equation if the total V changes after you add a substance! The concentrations will be lower due to dilution. (May use original M's if one V or no V is given - assume V is constant.)

You may either use the dilution formula to calc the new \(M_2's\) or you can calculate the moles (or mmoles) of each substance. For buffer problems, we always have a WA/WB mixture so the total V units cancel since we have a ratio of [base]/[acid] in either the HH equation or the \(K_a\) expression. Obviously, use the same units for all substances!

Moles \(\text{HCO}_2\text{H} = 500.0\text{mL} \times \frac{1\text{L}}{1000\text{mL}} \times \frac{0.10\text{mol}}{\text{L}} = 0.050\text{ moles } \text{HCO}_2\text{H} (or } M_2 = 0.0556 \text{ M } \text{HCO}_2\text{H})\)

Moles \(\text{HCO}_2^- = 400.0\text{mL} \times \frac{1\text{L}}{1000\text{mL}} \times \frac{0.20\text{mol}}{\text{L}} = 0.080\text{ moles } \text{HCO}_2^- (or } M_2 = 0.0889 \text{ M } \text{HCO}_2^-)\)

\[
pH = -\log K_a + \log \left(\frac{[\text{A}^-]}{[\text{HA}]}\right) \\
pH = -\log 1.8 \times 10^{-4} + \log (0.080/0.050)
\]

Key Common Ion, Buffer problems
\[ \text{pH} = 3.745 + 0.204 \quad \text{pH} = 3.95 \]

b) What is the pH after 20.0 mL of 0.50 M HCl is added to the buffer solution in part a?

strong acid: \( \text{HCl} + \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^- \)  

Have mixture of \( \text{H}_3\text{O}^+, \text{HCO}_2\text{H} \) and \( \text{HCO}_2^- \)

Strategy: Write AB neut rxn, calc moles & fill in ICF table, use amount of \( A^- \) and \( \text{HA} \) after neutralization in HH equation.

\( \text{SA} (\text{H}_3\text{O}^+) \) reacts with \( A^- (\text{HCO}_2^-) \): Neutralization rxn: \( \text{H}_3\text{O}^+ + \text{HCO}_2^- \rightarrow \text{HCO}_2\text{H} + \text{H}_2\text{O}(l) \)

\[ \Rightarrow \text{ Adding SA causes } A^- \text{ to be converted to } \text{HA} \text{ so } A^- \text{ goes to completion; its not equilibri} \]

From part a: Moles \( \text{HCO}_2\text{H} = 0.050 \) moles \( \text{HCO}_2\text{H} \)

Moles \( \text{HCO}_2^- = 0.080 \) moles \( \text{HCO}_2^- \)

From HCl: moles \( \text{H}_3\text{O}^+ = 0.0200 \text{ L} \times 0.50 \text{ M} = 0.010 \text{ mol } \text{H}_3\text{O}^+ \)

<table>
<thead>
<tr>
<th>Neutralization rxn</th>
<th>( \text{H}_3\text{O}^+ + \text{HCO}_2^- \rightarrow \text{HCO}_2\text{H} + \text{H}_2\text{O}(l) )</th>
</tr>
</thead>
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<tr>
<td>initial (mol)</td>
<td>0.010</td>
</tr>
<tr>
<td>Change (mol)</td>
<td>-0.010</td>
</tr>
<tr>
<td>Final (mol)</td>
<td>0.000</td>
</tr>
</tbody>
</table>

For ICF table: initial moles are calculated from moles = M\times L

Change: Reactants are consumed so subtract Limiting Reactant (smaller amount), Products are formed so add Limiting reactant.

Final = final moles after neutralization \( I + C = F \) (called final moles since a neutralization reaction goes to completion; its not equilibrium process).

\[ \text{pH} = -\log K_a + \log \left( \frac{[A^-]}{[HA]} \right) \quad \text{pH} = -\log 1.8 \times 10^{-4} + \log (0.070/0.060) \]

\[ \text{pH} = 3.745 + 0.067 \quad \text{pH} = 3.81 \checkmark \text{pH} \downarrow \text{ a little from 3.95 to 3.81 after SA added} \]

c) What is the pH after 20.0 mL of 0.50 M NaOH is added to the buffer solution is part a)

strong base: \( \text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^- \)  

Have mixture of \( \text{OH}^-, \text{HCO}_2\text{H} \) and \( \text{HCO}_2^- \)

Strategy: Write AB neut rxn, calc moles & fill in ICF table, use amount of \( A^- \) and \( \text{HA} \) after neutralization in HH equation.

\( \text{SB} (\text{OH}^-) \) reacts with \( \text{HA} (\text{HCO}_2\text{H}) \): Neutralization rxn: \( \text{OH}^- + \text{HCO}_2\text{H} \rightarrow \text{HCO}_2^- + \text{H}_2\text{O}(l) \)

\[ \Rightarrow \text{ Adding SB causes } \text{HA} \text{ to be converted to } A^- \text{ so } \text{HA} \downarrow \text{ and } A^- \uparrow \]

From part a: Moles \( \text{HCO}_2\text{H} = 0.050 \) moles \( \text{HCO}_2\text{H} \)

Moles \( \text{HCO}_2^- = 0.080 \) moles \( \text{HCO}_2^- \)

From NaOH: moles \( \text{OH}^- = 0.0200 \text{ L} \times 0.50 \text{ M} = 0.010 \text{ mol } \text{OH}^- \)

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\[ \text{pH} = -\log K_a + \log \left( \frac{[A^-]}{[HA]} \right) \quad \text{pH} = -\log 1.8 \times 10^{-4} + \log (0.090/0.040) \]

\[ \text{pH} = 3.745 + 0.352 \quad \text{pH} = 4.10 \checkmark \text{pH} \uparrow \text{ a little from 3.95 to 4.10 after SB added} \]

Key Common Ion, Buffer problems