Nuggets: Buffers: ID Buffer, Buffer Range/Capacity, pH of a Buffer, Add SA/SB to a Buffer-new pH, Prep of a Buffer

BUFFERS - resists change to pH; contains a weak acid + conjugate weak base in similar concentrations

- For a typical buffer, $[A^-]$ to $[HA]$ ratio is close to 1 and has a high concentration.
- $pK_a$ of the weak acid should be close to the desired pH of the buffer.
- A buffer works by converting a strong acid into a weak acid or a strong base into a weak base.

ID A BUFFER: Can be created from:
1. Weak Acid (WA) + salt of the Conjugate Base (similar amount of moles)
2. Weak Base (WB) + salt of the Conjugate Acid (similar amount of moles)
3. Weak Acid (WA) + Strong Base (SB) (if mol Strong Base < mol Weak Acid → is a buffer!)
4. Weak Base (WB) + Strong Acid (SA) (if mol Strong Acid < mol Weak Base → is a buffer!)

Example 1: Which of the following are buffers (not a multiple choice question)?

| a. 1-L of 1M CH₃COOH/1M NaCH₃COOH | b. 1-L of 1M HCl/1M NaCl | c. 1-L of 1M HBr/1M NaOH |
| d. 1-L of 1M HBr/0.5L of 1M NH₃ | e. 1-L of 1M HF/0.5L of 1M NaOH |

Answer 1: a, e {buffer = weak acid (WA) and conjugate weak base (WB) in comparable concentrations}

Shortcut: if mol WA > mol SB → is a buffer

For part “d” and “e” above: When a reaction includes a strong acid or a strong base the reaction will go to completion (100%) and the calculation is done in moles with a Start-Change-Finish (SCF) Table (not ICE Table) because equilibrium is not established (no "x" variables in SCF Table); in this reaction only one arrow (not equilibrium arrows) are used since no equilibrium is established.
CALCULATIONS INVOLVING BUFFERS
pH of a BUFFER: pH calculation: (any method below works; H-H equation is fastest!)

I. Henderson-Hasselbalch (H-H) equation: pH = pK_a + \log \left( \frac{[\text{base}]}{[\text{acid}]} \right) (must use pK_a not pK_b)

II. Weak acid reaction, ICE Table, K_a

III. Weak base reaction, ICE Table, K_b

Example 2: What is the pH of a 0.50M HF and 0.20M LiF solution? (K_a = 6.8 x 10^{-4})

Answer 2: Can solve problem with any of the 3 methods; use the H-H equation as it’s the fastest method!

Method 1: H-H eqn (fastest method; use this!)

<table>
<thead>
<tr>
<th>Step 1: H-H equation</th>
<th>Step 2: Plug into H-H equation</th>
<th>Step 3: Make approximation and solve for x</th>
<th>Step 4: Determine pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH = pK_a + \log \left( \frac{[\text{base}]}{[\text{acid}]} \right)</td>
<td>pH = -\log(6.8\times10^{-4}) + \log \left( \frac{0.20}{0.50} \right) = 2.77</td>
<td>6.8\times10^{-4} = \frac{(x)(0.20+x)}{(0.50-x)}; x = 1.70 \times 10^{-3}</td>
<td>pH = -\log[H_3O^+] = -\log(1.70 \times 10^{-3}) = 2.77</td>
</tr>
</tbody>
</table>

Method 2: Weak acid/K_a

<table>
<thead>
<tr>
<th>Step 1: ICE Table</th>
<th>Step 2: Plug into K_a</th>
<th>Step 3: Make approximation and solve for x</th>
<th>Step 4: Determine pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF + H_2O \rightleftharpoons H_3O^+ + F^-</td>
<td>K_a = \frac{[H_3O^+][F^-]}{[HF]} = \frac{(x)(0.20+x)}{(0.50-x)}</td>
<td>6.8 \times 10^{-4} = \frac{(0.50+x)(x)}{(0.50-x)}; x = 1.70 \times 10^{-3}</td>
<td>pH = -\log[H_3O^+] = -\log(1.70 \times 10^{-3}) = 2.77</td>
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</table>

Method 3: Weak base/K_b

<table>
<thead>
<tr>
<th>Step 1: ICE Table</th>
<th>Step 2: Determine K_b and plug into K_b</th>
<th>Step 3: Make approximation and solve for x</th>
<th>Step 4: Determine pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>F^- + H_2O \rightleftharpoons HF + OH^-</td>
<td>K_b = \frac{[HF][OH^-]}{[F^-]} = \frac{(0.50+x)(x)}{(0.20-x)}</td>
<td>1.47 \times 10^{-11} = \frac{(0.50+x)(x)}{(0.20-x)}; x = 5.88 \times 10^{-12}</td>
<td>pH = -\log[OH^+] = -\log(5.88 \times 10^{-12}) = 11.23</td>
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</tbody>
</table>

pH = 14 − 11.23 = 2.77

Deriving the Henderson-Hasselbalch (H-H) Equation

1. Weak acid: HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)

2. Write K_a expression: K_a = \frac{[H_3O^+][A^-]}{[HA]}

3. Take -log of both sides: −logK_a = -\log \left( \frac{[H_3O^+][A^-]}{[HA]} \right)

4. Split the log argument: −logK_a = -\log \left( \frac{[H_3O^+]}{1} \right) + \log \left( \frac{[A^-]}{[HA]} \right)

5. Pull apart the log argument: −logK_a = −log[H_3O^+] + \left( −\log \frac{[A^-]}{[HA]} \right)

6. Rearrange equation: −log[H_3O^+] = −logK_a + log \left( \frac{[A^-]}{[HA]} \right)

7. Make substitutions: pH = −log[H_3O^+]; pK_a = −log(K_a)

pH = pK_a + log \left( \frac{[A^-]}{[HA]} \right) (H-H eqn)
REACT ON OF A BUFFER WITH A STRONG ACID OR STRONG BASE - pH calculations

When a buffer reacts with a strong acid/base, the problem is done in two parts.

**Part I:** the SA/SB reacts with the buffer. When a reaction includes a strong acid or a strong base the reaction will go to completion (100%) and the calculation is done in moles with a Start-Change-Finish (SCF) Table (not ICE Table) because equilibrium is not established (no "x" variables in SCF Table); in this reaction only one arrow (not equilibrium arrows) are used since no equilibrium is established.

**Step 1:** Find all moles; write reaction (SA + WB reaction or SB + WA reaction)
**Step 2:** Do SCF Table (Start, Change, Finish) in moles; goes to completion (100%)

**Part II:** after the reaction is complete the buffer’s number of moles has changed due to the acid/base reaction; the pH of the buffer is determined in one of the above three ways (H-H is fastest; use this!).

**Step 3:** H-H equation: \[ \text{pH} = -\log \left( \frac{\text{base}}{\text{acid}} \right) \]

**Example:** a. What is the pH of a buffer containing 0.500M HCOOH and 0.750M HCOONa solution? (\(K_a \text{ HCOOH} = 1.8 \times 10^{-5}\))

**Answer:** a. Since a buffer exists \(\rightarrow\) use H–H equation: \[ \text{pH} = -\log \left( \frac{0.750}{0.500} \right) = 3.92; \text{pH} = 3.92 \]

**Step 1:** Find mol of all chemicals
- mol NaOH: 5.0g NaOH \(\frac{\text{mol NaOH}}{40.0g \text{NaOH}}\) = 0.125mol NaOH
- mol HCOOH: \(M \times L = (0.50M)(0.50L) = 0.250\text{mol HCOOH}\)
- mol HCOONa: \(M \times L = (0.75M)(0.50L) = 0.375\text{mol HCOONa}\)

**Write reaction of SB with WA:**
\[ \text{OH}^-(aq) + \text{HCOOH}(aq) \rightarrow \text{HCOO}^-(aq) + \text{H}_2\text{O}(l) \]
Using 1 arrow implies reaction goes to completion (100%)  

**Step 2:** Write SCF Table in mol; since SB is present 1 arrow \(\rightarrow\) goes to completion:

<table>
<thead>
<tr>
<th></th>
<th>S</th>
<th>C</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH(^-)(aq)</td>
<td>0.125</td>
<td>-0.125</td>
<td>0.125</td>
</tr>
<tr>
<td>HCOOH(aq)</td>
<td>0.250</td>
<td>-0.125</td>
<td>0.500</td>
</tr>
<tr>
<td>HCOO(^-)(aq)</td>
<td>0.375</td>
<td>+0.125</td>
<td>---</td>
</tr>
<tr>
<td>H(_2)O(l)</td>
<td>---</td>
<td>---</td>
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</tr>
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</table>

**Part II:** find pH of the new buffer
**Step 3:** use H–H equation
\[ \text{pH} = -\log \left( \frac{0.500}{0.125} \right) = 4.35 \]

Note that pH went up from 3.92 which is expected since a base was added; that is, add a base and pH goes up.

**Why can you use** \(\frac{\text{mol base}}{\text{mol acid}}\) instead of \(\frac{\text{base}}{\text{acid}}\)?

\[ \text{mol base} = 0.500\text{mol} \]
\[ \text{mol acid} = 0.125\text{mol} \]
\[ \frac{\text{mol base}}{\text{mol acid}} = 4 \]
\[ \frac{\text{base}}{\text{acid}} = \frac{(0.500\text{mol} / 0.50L)}{(0.125\text{mol} / 0.50L)} = 1.00 \]
\[ \text{pH} = 4 \]
BUFFER pH RANGE/CHOOSING A BUFFER: \( \text{pH} = \text{pK}_a \pm 1 \)

The ratio of \([\text{base}] : [\text{acid}]\) must be in the range of 10 : 1 or 1 : 10. If the ratio is larger than that, e.g., [base] = 100 x [acid], the solution no longer acts as a buffer! This can also be described as:

\[
\frac{1}{10} \leq \frac{[\text{weak base}]}{[\text{weak acid}]} \leq 10 \quad \text{or} \quad 0.1 \leq \frac{[\text{weak base}]}{[\text{weak acid}]} \leq 10
\]

This information can be used to choose a buffer from a series of solutions for a desired pH

Deriving \( \text{pH} = \text{pK}_a \pm 1 \)

Use the H-H equation first with a 10 : 1 ratio: \([\text{base}] = 10 \) and \([\text{acid}] = 1 \) to yield: \( \text{pH} = \text{pK}_a + \log \left( \frac{10}{1} \right) = \text{pK}_a + 1 \)

Now repeat with a 1 : 10 ratio: \([\text{base}] = 1 \) and \([\text{acid}] = 10 \) to yield: \( \text{pH} = \text{pK}_a + \log \left( \frac{1}{10} \right) = \text{pK}_a - 1 \)

Hence, the pH range of a buffer that maintains a \([\text{base}] : [\text{acid}]\) ratio of 1 : 10 through 10 : 1 is: \( \text{pH} = \text{pK}_a \pm 1 \)

Example 4: A buffer with \( \text{pH} \approx 3 \) was desired. Which buffer below would be the best choice?

a. 1.0-L of 1.0M CH₃COOH/1.0M NaCH₃COO \( (\text{K}_a = 1.8 \times 10^{-5}) \)

b. 1.0-L of 1.0M HNO₂/1.0M KNO₂ \( (\text{K}_a = 7.4 \times 10^{-4}) \)

c. 1.0-L of 1.0M CH₃NH₂/1.0M CH₃NH₂ \( (\text{K}_b = 5.0 \times 10^{-4}) \)

Answer 4: b. 1M HNO₂/1M KNO₂

\{determine \text{pK}_a \text{ and then the pH range of each buffer; \}

Choice a: \( \text{pK}_a = -\log(1.8 \times 10^{-5}) = 4.74 \), buffer pH range = \( \text{pK}_a \pm 1 = 4.74 \pm 1 = 3.74 \) to 5.74;

Choice b: \( \text{pK}_a = -\log(7.4 \times 10^{-4}) = 3.13 \), buffer pH range = \( \text{pK}_a \pm 1 = 3.13 \pm 1 = 2.13 \) to 4.13;

Choice c: \( \text{pK}_b = -\log(5.0 \times 10^{-4}) = 3.30 \); \( \text{pK}_a = 14 - \text{pK}_b = 14 - 3.30 = 10.70 \), buffer pH range = \( \text{pK}_a \pm 1 = 10.70 \pm 1 = 9.70 \) to 11.70; note that the \( \text{pK}_b \) is used not the \( \text{pK}_b \);

only the 1.0M HNO₂/1.0M KNO₂ buffer has a pH range that encompasses the desired pH of ~3!}

BUFFER CAPACITY: The amount of strong acid/strong base a buffer can accommodate before it is depleted.

- If solution pH is outside of buffer pH range (\( \text{pK}_a \pm 1 \)) buffer capacity has been exceeded and the buffer is depleted.
- As the number of moles weak acid and weak base increase in a buffer, the greater the buffer capacity.

Example 5: A 750ml buffer contains 0.40M HF and 0.65M NaF, and 15.0g HCl are added to the buffer. Has the buffer capacity been exceeded and the buffer depleted? \( \text{K}_a \text{ HF} = 6.8 \times 10^{-4} \)

Answer 5: Buffer capacity has not been exceeded and buffer is not depleted (just barely) \{Find new pH after HCl has been added; start by writing a reaction, \( \text{H}_2\text{O}^+(aq) + \text{F}^-(aq) \rightarrow \text{HF}(aq) + \text{H}_2\text{O}(l) \); find all mol present; mol HF = M x L = (0.40M)(0.75L) = 0.30mol HF;

mol \( \text{F}^- = \text{M} \times \text{L} = (0.65M)(0.75L) = 0.488mol \text{ F}^- \); mol HCl = 15.0g HCl x (1mol HCl/36.5g HCl) = 0.411mol HCl;

write SCF Table and then use H-H equation to find pH;

\[
\begin{align*}
\text{F}^- & : 0.488 & 0.411 & 0.300 & \cdots \\
\text{C} & : -0.411 & -0.411 & +0.411 & +0.411 \\
\text{F} & : 0.077 & 0 & 0.711 & \cdots \\
\end{align*}
\]

\( \text{pK}_a = -\log(6.8 \times 10^{-4}) = 3.17; \text{pH} = \text{pK}_a + \log \left( \frac{[\text{base}]}{[\text{acid}]} \right); \text{pH} = 3.17 + \log \left( \frac{0.077}{0.711} \right) = 2.20; \text{the effective pH range of a buffer} = \text{pK}_a \pm 1; \)

for this buffer, the effective range is: \( 3.17 \pm 1 = 2.17 \text{ -- 4.17; since the pH of the solution after the addition of the HCl which is 2.20 is still within the effective pH range of the buffer, the buffer capacity has not been exceeded and the buffer has not been depleted (though just barely!)} \}
**PREPARATION OF A BUFFER:**

1. Buffer can be “given” to you; e.g., 0.5M CH₃COOH and 0.3M NaCH₃COOH
2. Buffer can be given as SA/WB or WA/SB; e.g., 0.40g NaOH(s) and 100.m 0.50M CH₃COOH; write reaction and SCF Table in mol; e.g., CH₃COOH(aq) + OH⁻(aq) → H₂O(l) + CH₃COO⁻(aq);

\[
\begin{array}{ccc}
S & 0.050 & 0.010 \\
C & -0.010 & +0.010 \\
F & 0.040 & 0 \\
\end{array}
\]

\[\text{[CH₃COOH]} = 0.040\text{mol/0.100L} = 0.40M; \text{[CH₃COO}^-] = 0.010\text{mol/0.100L} = 0.10M\]

then use the H–H equation to find pH

3. Buffer can have 2 solutions that are mixed; e.g., 100.ml 0.10M HF and 200.ml 0.20M NaF; need to find either new concentrations of WA and WB (M₁V₁ = M₂V₂) or find moles WA and moles WB;

\[\text{[HF]}: (0.10M)(100.\text{ml}) = M2(100. + 200.); \text{[HF]} = 0.033M; \text{[F}^-]: (0.20M)(200.\text{ml}) = M2(100. + 200.); \text{[F}^-] = 0.13M;\]

or can just find moles: mol HF = (0.10M)(0.100L) = 0.010mol; mol F⁻ = (0.20M)(0.200L) = 0.040mol;

then use the H–H equation to find pH

4. Can also be asked to determine an amount of one chemical to add to achieve a certain buffer; use H–H equation (see examples below)

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**Example 6:** How many grams of NaHCOO must be added to a 1.50L of 0.75M HCOOH solution to create a buffer with a pH = 3.40? \(K_a = 3.0 \times 10^{-4}\)

**Answer 6:** 58.1g NaHCOO  

\[\text{Use the H–H equation: } \text{pH} = pK_a + \log \left( \frac{\text{base}}{\text{acid}} \right) \text{; find } pK_a = \log(3.0 \times 10^{-4}) = 3.52; \]

plug into H–H equation: \(3.40 = 3.52 + \log \left( \frac{\text{NaHCOO}}{0.75} \right) \text{; solve for } \text{[NaHCOO]}: -0.12 = \log \left( \frac{\text{NaHCOO}}{0.75} \right) ; 10^{-0.12} = \frac{\text{NaHCOO}}{0.75} ; \]

\[\text{grams NaHCOO} = 0.854 \text{mol NaHCOO} \times \frac{68.08\text{g NaHCOO}}{1\text{mol NaHCOO}} = 58.13\text{g NaHCOO} \}

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**Example 7:** How many grams of NaOH must be added to a 1.50L of 0.75M HCOOH solution to create a buffer with a pH = 3.40? \(K_a = 3.0 \times 10^{-4}\)

(This is the same question as Example 6 except a strong base, NaOH, is added instead of the conjugate weak base which makes this question more complicated.)

**Answer 7:** 19.4g NaOH  

\[\text{Start by writing a reaction: } \text{HCOOH(aq)} + \text{OH}^- (aq) \rightarrow \text{HCOO}^- (aq) + \text{H}_2\text{O(l)} ; \]

\[
\begin{array}{ccc}
S & 1.125 & x \\
C & -x & -x \\
F & 1.125-x & 0 \\
\end{array}
\]

\[\text{find mol HCOOH} = M \times L = (0.75M)(1.5L) = 1.125 \text{mol HCOOH} ; \text{write SCF Table; Note that in this case there are } \text{“x”} \text{ values in the SCF Table which is not typical;} \]

\[\text{use the H–H equation: } \text{pH} = pK_a + \log \left( \frac{\text{base}}{\text{acid}} \right) ; \text{ find } pK_a = \log(3.0 \times 10^{-4}) = 3.52; \]

plug into H–H equation (note: mol rather than M is being plugged into the H–H equation): \(3.40 = 3.52 + \log \left( \frac{x}{1.125-x} \right) ; \]

solve for \(x\): \(-0.12 = \log \left( \frac{x}{1.125-x} \right) ; 10^{-0.12} = \frac{x}{1.125-x} ; 0.759 = \frac{x}{1.125-x} ; \text{cross multiply: } 0.8539 - 0.759x = x; \]

collect \(x\) terms: \(0.8539 = 1.759x; x = 0.485; x\) represents the mol of NaOH added, the mol of HCOO⁻ created, and the mol of HCOOH that reacted with the NaOH; using 0.485mol NaOH find grams NaOH: \(\frac{40.0g \text{ NaOH}}{1\text{mol NaOH}} \times 0.485 \text{mol NaOH} = 19.4g \text{ NaOH} \}
1. When 1.0 L of each of the solutions below are mixed, which will form a buffer? (Not a multiple choice question; there may be more than one buffer present.)
   a. 1.0 M HF + 0.50 M F⁻
   b. 0.10 M HCN + 0.10 M NaCN
   c. 0.025 M HCl + 0.025 M NaCl
   d. 0.10 M HCl + 0.50 M NaOH
   e. 0.25 M NH₃ + 0.50 M NH₄⁺
   f. 0.50 M NH₃ + 0.25 M HCl

2. What happens to the [H₃O⁺] when NaF is added to a 0.1M HF solution?
   a. Increases.
   b. Decreases.
   c. Remains unchanged.
   d. Since NaF is the conjugate base of HF, it is not possible to determine without the concentrations of each component being given.
   e. None of the above.

3. If a student needed to prepare a buffered solution with pH ≈ 5, which buffer would be the best choice?
   a. 1L of 1M CH₃COOH/1M NaCH₃COO (Kₐ = 1.8 x 10⁻⁵)
   b. 1L of 1M HF/1M NaF (Kₐ = 7.2 x 10⁻⁴)
   c. 1L of 1M HCOOH/NaHCOO (Kₐ = 1.8 x 10⁻⁴)
   d. 1L of 1M HOCl/NaOCl (Kₐ = 3.5 x 10⁻⁸)
   e. 1L of 1M HCN/1M NaCN (Kₐ = 4.0 x 10⁻¹⁰)

4. Which buffer would be the best choice to create the lowest pH buffer range? (Harder version of Question 3)
   a. NaHCO₃(aq)/Na₂CO₃(aq) (Kₐ₁ = 4.3 x 10⁻⁷; Kₐ₂ = 4.7 x 10⁻¹¹)
   b. CH₃NH₃Cl(aq)/CH₃NH₂(aq) (Kₐ = 5.0 x 10⁻⁴)
   c. NaH₂PO₄(aq)/Na₂HPO₄(aq) (Kₐ₁ = 7.2 x 10⁻³; Kₐ₂ = 6.3 x 10⁻⁸; Kₐ₃ = 4.6 x 10⁻¹³)
   d. HCN(aq)/NaCN(aq) (Kₐ = 3.3 x 10⁻¹⁰)
   e. NH₄Cl(aq)/NH₃(aq) (Kₐ₈ = 1.8 x 10⁻⁵)

5. To a hydrofluoric acid solution, HF(aq), lithium fluoride, LiF(aq), is added. Which of the following statements is correct?
   a. The F⁻(aq) will react with the HF(aq) and pH will increase.
   b. The equilibrium will favor the formation of F⁻(aq) and pH will decrease.
   c. The F⁻(aq) will react with H₃O⁺ and the pH will decrease.
   d. The F⁻(aq) will create OH⁻(aq) and the pH will increase.
   e. The change in pH can only be determined if the concentrations are known.

6. The pKₐ of the buffer HCO₃⁻/H₂CO₃ is 6.38. To obtain a pH of 6.50, which of the following is correct?
   a. [HCO₃⁻] > [H₂CO₃]
   b. [HCO₃⁻] = [H₂CO₃]
   c. [HCO₃⁻] < [H₂CO₃]
   d. The Kₐ is needed to solve this question

7. a. What is the pH of a solution that contains 1.00M HCN and 0.75M NaCN (Kₐ of HCN = 6.2 x 10⁻¹⁰)?
   b. What is the pH of a solution that contains 0.10M NH₃ and 0.25M NH₄⁺ (Kᵇ of NH₃ = 1.8 x 10⁻⁵)?
8. What is the pH of a buffer when 20.0g NaCH₃COO(s) is added to 1.0L 0.50M CH₃COOH? Assume the volume of the solution does not change when the solid is added. (Kₐ of CH₃COOH = 1.8 x 10⁻⁵)

9. a. What is the pH of a 1.0L solution of 0.50M CH₃COOH (Kₐ = 1.8 x 10⁻⁵)? (Hint: This is not a buffer.)
b. 4.0g of NaOH are now added to the above solution. Write the reaction that occurs with the NaOH.
c. What is the final pH of the new solution after the NaOH has been added? (Hint: Now it’s a buffer.) Assume the volume of the solution does not change when the solid is added.

10. a. What is the pH of a 300.ml buffered solution containing 0.055M NaCH₃COO and 0.125M CH₃COOH? (Kₐ CH₃COOH = 1.8 x 10⁻⁵)
b. To this solution 0.45g NaOH is added; what is the new pH of the solution?

11. a. What is the pH of a 650.ml buffered solution containing 0.150M HNO₂ and 0.250M NaNO₂? (Kₐ HNO₂ = 4.5 x 10⁻⁴)
b. To this solution 2.28g HCl is added; what is the new pH of the solution?

12. a. A 250ml 0.20M NH₃ solution is mixed with 150ml 0.25M NH₄Cl solution. What is the pH of the new solution? (Kᵦ NH₃ = 1.8 x 10⁻⁵)
b. To this solution 1.26g HNO₃ is added. Write the net ionic reaction that occurs. What is the new pH of the solution?

13. A 1.0-L buffer solution containing 0.50M H₂CO₃ and 0.75M NaHCO₃ is prepared. a. What is the pH of the buffer? b. If 4.0g NaOH is added, what is the new pH? (Kₐ₁ = 4.2 x 10⁻⁷; Kₐ₂ = 4.8 x 10⁻¹¹)

**Buffer Preparation**

14. A NH₃/NH₄⁺ buffer was to be prepared with a pH of 9.45.
a. What concentration of NH₃ is needed if the concentration of NH₄⁺ is 1.15M? (Kᵦ NH₃ = 1.8 x 10⁻⁵)
b. If the volume of the solution is 2.50L, how many grams of NH₃ must be dissolved into the solution?

15. How much NaCH₃COO(s) must be added to 1.5L 0.25M CH₃COOH to obtain a buffer solution with a pH of 4.95? (Kₐ = 1.8 x 10⁻⁵)

16. What volume of 0.50M NaOH must be added to 1.0L of 1.0M C₆H₅COOH (Kₐ = 6.3 x 10⁻⁵) to obtain a buffer with a pH = 4.45?

17. How much volume of 0.75M HCl must be added to 1.0L of 0.5M NH₃ (Kᵦ = 1.8 x 10⁻⁵) to obtain a buffer with a pH = 9.50?
**Buffer Capacity**

18. Given the following four buffer solutions, answer the two questions below?
   i. 10.0ml of 1.0M HNO₂(aq), 2.0M NaNO₂(aq)
   ii. 100.0ml of 0.20M HNO₂(aq), 0.40M NaNO₂(aq)
   iii. 100.0ml of 1.0M HNO₂(aq), 2.0M H NaNO₂(aq)
   iv. 100.0ml of 0.10M HNO₂(aq), 0.20M NaNO₂(aq)

I. Which solution will have the greatest buffer capacity? (Hint: no calculation is needed.)
   a. i b. ii c. iii d. iv e. all have the same buffer capacity

II. Which solution will have the lowest pH? (Hint: no calculation is needed.)
   a. i b. ii c. iii d. iv e. all have the same pH

**ANSWERS**

1. a, b, e, f  
   {“a” is a buffer-WA/WB; “b” is a buffer-WA/WB; “c” is not a buffer-SA/neutral salt; “d” is not a buffer-SA/SB; “e” is a buffer-WA/WB; “f” is a buffer – set up SCF Table using this reaction: \( \text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+ \); Final: mol NH₃ = 0.25; mol NH₄⁺ = 0.25 → WA/WB present}

2. b  
   {adding NaF which is a base \( \rightarrow \) more basic \( \rightarrow [\text{H}_3\text{O}^+] \) \( \downarrow \); or Le Chatelier’s Principle: \( \text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^- \); when \( \text{F}^- \) is added from NaF, this drives the reaction to the left which uses up the \( \text{H}_3\text{O}^+ \) and [\( \text{H}_3\text{O}^+ \) \( \downarrow \)]}

3. a  
   {the pH = pKₐ of a buffer when the [HA] = [A⁻]; calculate pKₐ for each of the above and the CH₃COOH/NaCH₃COO is closest to 5}

4. c  
   {the pH buffer range is: pH = pKₐ \( \pm 1 \); calculate pKₐ \( \pm 1 \) for each buffer:}
   a) for this acid/base mixture and using:
      \[
      \begin{align*}
      \text{H}_2\text{CO}_3 & \rightleftharpoons \text{HCO}_3^- & \text{HCO}_3^- & \rightleftharpoons \text{CO}_3^{2-}
      \end{align*}
      \]
      the solution mixture is represented by pKₐ₂: pKₐ₂ = 10.33, range: 9.33 \( \leftrightarrow \) 11.33;
   b) pKₐ = 3.30 so pKₐ = 10.70, range: 9.70 \( \leftrightarrow \) 11.70;
   c) for this acid/base mixture and using:
      \[
      \begin{align*}
      \text{H}_3\text{PO}_4 & \rightleftharpoons \text{H}_2\text{PO}_4^- & \text{H}_2\text{PO}_4^- & \rightleftharpoons \text{HPO}_4^{2-} & \text{HPO}_4^{2-} & \rightleftharpoons \text{PO}_4^{3-}
      \end{align*}
      \]
      the solution mixture is represented by pKₐ₂; pKₐ₂ = 7.20, range: 6.20 \( \leftrightarrow \) 8.20;
   d) pKₐ = 9.48, range: 8.48 \( \leftrightarrow \) 10.48;
   e) pKₐ = 4.74 so pKₐ = 9.26, range: 8.26 \( \leftrightarrow \) 10.26; the lowest buffer range is from NaH₃PO₄(aq)/Na₂HPO₄(aq)}

5. d  
   {F⁻(aq) + \( \text{H}_2\text{O}(l) \) \( \rightleftharpoons \) HF(aq) + OH⁻(aq) and the pH will increase since OH⁻ is being created; another way this can be described is: \( \text{F}^-\text{(aq)} + \text{H}_3\text{O}^+(\text{aq}) \rightleftharpoons \text{HF}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \) and as the \( \text{H}_3\text{O}^+ \) is consumed the pH will increase; finally this can be thought of as a Le Chatelier’s Principle question: \( \text{HF}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{F}^-\text{(aq)} + \text{H}_3\text{O}^+(\text{aq}) \) as \( \text{F}^- \) is added the reaction shifts to the left and the amount of \( \text{H}_3\text{O}^+ \) decreases thereby increasing the pH}

6. a  
   {to bring pH up from the pKₐ need to add base; mathematically, need \( \log \frac{[\text{base}]}{[\text{acid}]} \) to be positive \( \rightarrow [\text{base}] > [\text{acid}] \)}
7. a. pH = 9.08  {use H–H equation: pH = pK_a + log \frac{[base]}{[acid]}; pH = -log(6.2 \times 10^{-10}) + log \left( \frac{0.75}{1.00} \right) = 9.08 } \\
b. pH = 8.86  {find K_a from K_a = K_w/K_b = 1.0 \times 10^{-14}/1.8 \times 10^{-5} = 5.56 \times 10^{-10}; use H–H equation: pH = pK_a + log \frac{[base]}{[acid]};} \\
\text{pH} = -log(5.56 \times 10^{-10}) + log \left( \frac{0.10}{0.25} \right) = 8.86 \\
8. pH = 4.43  {\text{[NaCH}_3\text{COO]} = 0.243\text{mol/1.0L = 0.243M; pH = pK}_a + \log \frac{[base]}{[acid]}; \text{pH} = -log(1.8 \times 10^{-5}) + log \left( \frac{0.243}{0.50} \right) = 4.43 } \\
9. a. pH = 2.52  {\text{WA problem; CH}_3\text{COOH(aq) + H}_2\text{O(l) } \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{COO}^-(aq); write ICE Table;} \\
\text{K}_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}; 1.8 \times 10^{-5} = \frac{(x)(x)}{(0.50 - x)} = \frac{x^2}{0.50 - x}; \text{check for approximation: (100)}K_a < [\text{HA}]_0; \\
100(1.8 \times 10^{-5}) = 1.8 \times 10^{-3} < 0.50 \rightarrow \text{make approximation: } 1.8 \times 10^{-5} = \frac{x^2}{0.50}; x = 0.00300 = [\text{H}_3\text{O}^+]; \text{pH} = -log(0.003) = 2.52 } \\
b. \text{CH}_3\text{COOH(aq) + OH}^-\text{(aq) } \rightarrow \text{CH}_3\text{COO}^-\text{(aq) + H}_2\text{O(l)} \text{ (or CH}_3\text{COOH(aq) + NaOH(aq) } \rightarrow \text{CH}_3\text{COONa(aq) + H}_2\text{O(l))} \\
c. pH = 4.14  {\text{CH}_3\text{COOH(aq) + OH}^-\text{(aq) } \rightarrow \text{H}_2\text{O(l) + CH}_3\text{COO}^-\text{(aq)};} \\
\text{mol NaOH: 4.0g NaOH } \left( \frac{1\text{mol NaOH}}{40.0g \text{NaOH}} \right) = 0.10\text{mol NaOH} ; \\
\text{mol CH}_3\text{COOH} = M \times L = (0.50M)(1.0L) = 0.5\text{mol CH}_3\text{COOH}; \text{write SCF Table; WA/WB present } \rightarrow \text{have a buffer; use H–H equation:} \\
\text{pH = pK}_a + \log \frac{[base]}{[acid]}; \text{pH} = -log(1.8 \times 10^{-5}) + log \left( \frac{0.10}{0.40} \right) = 4.14 } \\
10. a. pH = 4.39  {\text{use H–H equation: pH = pK}_a + \log \frac{[base]}{[acid]}; pH = -log(1.8 \times 10^{-5}) + log \left( \frac{0.055}{0.125} \right) = 4.388 } \\
b. pH = 4.77  {\text{Part I: CH}_3\text{COOH(aq) + OH}^-\text{(aq) } \rightarrow \text{CH}_3\text{COO}^-\text{(aq) + H}_2\text{O(l); write SCF Table;} \\
\text{mol CH}_3\text{COOH} = M \times L = (0.125M)(0.3L) = 0.0375\text{mol CH}_3\text{COOH;} \\
\text{mol NaOH: 0.45g NaOH } \left( \frac{1\text{mol NaOH}}{40.0g \text{NaOH}} \right) = 0.01125\text{mol NaOH} ; \\
\text{mol CH}_3\text{COO}^- = M \times L = (0.055M)(0.300L) = 0.0165\text{mol CH}_3\text{COO}^-; \text{Part II: use H–H equation: pH = pK}_a + \log \frac{[base]}{[acid]}; \text{pH} = -log(1.8 \times 10^{-5}) + log \left( \frac{0.02775}{0.02625} \right) = 4.769 }
11. a. pH = 3.57  
\{use H–H equation: \( pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]} \); \( pH = -\log(4.5 \times 10^{-4}) + \log\left(\frac{0.25}{0.15}\right) = 3.569 \} \]

b. pH = 3.14  
\{Part I: \( \text{NO}_2^- (aq) + \text{H}_3\text{O}^+ (aq) \rightarrow \text{HNO}_2 (aq) + \text{H}_2\text{O}(l) \); \( \text{mol NO}_2^- = M \times L = (0.25)(0.65) = 0.1625\text{mol NO}_2^- \); \( \text{mol HCl} \): \( 2.28\text{g HCl} \times \frac{1\text{mol HCl}}{36.46\text{g HCl}} = 0.0625\text{mol HCl} = 0.0625\text{mol H}_3\text{O}^+ \); \( \text{mol HNO}_2 = M \times L = (0.15\text{M})(0.65\text{L}) = 0.0975\text{mol HNO}_2 \); write SCF Table; Part II: use H–H equation: \( pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]} \); \( pH = -\log(4.5 \times 10^{-4}) + \log\left(\frac{0.1000}{0.1600}\right) = 3.143 \} \]

12. a. 9.38  
\{a buffer since it contains a WA and WB; use H–H equation; can use mol or M in H–H equation; will use mol since the next question adds a SA and it will also need mol; \( \text{mol NH}_3 = M \times L = (0.20)(0.25) = 0.050\text{mol} \); \( \text{mol NH}_4^+ = M \times L = (0.25\text{M})(0.15\text{L}) = 0.0375\text{mol} \); \( K_a = 1.0 \times 10^{-14} / 1.8 \times 10^{-5} = 5.56 \times 10^{-10} \); \( pH = -\log(5.56 \times 10^{-10}) + \log\left(\frac{0.050}{0.0375}\right) = 9.38 \} \]

b. 8.97  
\{Part I: net ionic reaction: \( \text{NH}_3(aq) + \text{H}_3\text{O}^+(aq) \rightarrow \text{NH}_4^+(aq) + \text{H}_2\text{O}(l) \); \( \text{mol HNO}_3 \): \( 1.26\text{g HNO}_3 \times \frac{1\text{mol HNO}_3}{63.0\text{g HNO}_3} = 0.020\text{mol HNO}_3 = 0.020\text{mol H}_3\text{O}^+ \); write SCF Table; Part II: use H–H equation: \( pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]} \); \( pH = -\log(5.56 \times 10^{-10}) + \log\left(\frac{0.030}{0.0575}\right) = 8.97 \} \]

13. a. 6.55  
\{\( \text{H}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3^-(aq) + \text{H}_3\text{O}^+(aq) \) corresponds to \( K_{a1} \) since the first \( \text{H}^+ \) is coming off; use H–H equation: \( pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]} \); \( pH = -\log(4.2 \times 10^{-7}) + \log\left(\frac{0.75}{0.50}\right) = 6.55 \} \]

b. 6.70  
\{Part I: \( \text{H}_2\text{CO}_3(aq) + \text{OH}^-(aq) \rightarrow \text{HCO}_3^-(aq) + \text{H}_2\text{O}(l) \); \( \text{mol H}_2\text{CO}_3 = M \times L = (0.50)(1) = 0.50\text{mol H}_2\text{CO}_3 \); \( \text{mol NaOH} \): \( 4.00\text{g NaOH} \times \frac{1\text{mol NaOH}}{40.0\text{g NaOH}} = 0.10\text{mol NaOH} \); \( \text{mol HCO}_3^- = M \times L = (0.75\text{M})(1.0\text{L}) = 0.75\text{mol HCO}_3^- \); write SCF Table; Part II: use H–H equation: \( pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]} \); \( pH = -\log(4.2 \times 10^{-7}) + \log\left(\frac{0.85}{0.40}\right) = 6.70 \} \]
14. a. 1.82M \{buffer prep \rightarrow use \text{H-H equation: } pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]};
K_a = 1.0 \times 10^{-14}/K_b = 1.0 \times 10^{-14}/1.8 \times 10^{-5} = 5.56 \times 10^{-10}; \ pH = 9.45; [\text{acid}] = [\text{NH}_4^+] = 1.15M;
9.45 = -\log(5.56 \times 10^{-10}) + \log \left( \frac{[\text{NH}_3]}{1.15} \right); \ 9.45 = 9.25 + \log \left( \frac{[\text{NH}_3]}{1.15} \right); \ 0.20 = \log \left( \frac{[\text{NH}_3]}{1.15} \right); \ 10^{0.20} = 10 \log \left( \frac{[\text{NH}_3]}{1.15} \right);
1.58 = \left[ \text{NH}_3 \right]/1.15; \ [\text{NH}_3] = 1.817M \}

b. 77.4g \text{NH}_3 \{M = \text{mol/L}; \ 1.817M = \text{mol/2.50L}; \ \text{mol} \text{NH}_3 = 4.54\text{mol} \text{NH}_3; \ 4.54\text{mol} \text{NH}_3 \left( \frac{17.03g \text{NH}_3}{1\text{mol} \text{NH}_3} \right) = 77.36g \text{NH}_3 \}

15. 49.9g \text{NaCH}_3\text{COO} \text{ are needed} \{use \text{H-H equation: } pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]};
4.95 = -\log(1.8 \times 10^{-5}) + \log \left( \frac{[\text{base}]}{0.25} \right); \ 4.95 = 4.74 + \log \left( \frac{[\text{base}]}{0.25} \right); \ 0.21 = \log \left( \frac{[\text{base}]}{0.25} \right); \ 10^{0.21} = 10 \log \left( \frac{[\text{base}]}{0.25} \right);
1.62 = \frac{[\text{base}]}{0.25}; \ [\text{base}] = 0.405M; \ \text{find mol: } M \times L = \text{mol}; \ 0.405M \times 1.5L = 0.608mol;
\text{find grams: } 0.608mol \text{NaCH}_3\text{COO} \left( \frac{82.03g \text{NaCH}_3\text{COO}}{1\text{mol} \text{NaCH}_3\text{COO}} \right) = 49.88g \text{NaCH}_3\text{COO} \}

16. 1.3L of 0.50M \text{NaOH} \{\text{Part I. Rxn: } \text{C}_6\text{H}_5\text{COOH}(aq) + \text{OH}^- (aq) \rightarrow \text{C}_6\text{H}_5\text{COO}^- (aq) + \text{H}_2\text{O}(l); \ \text{write SCF Table;}
\text{Part II: use H-H equation: } pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]};
\text{C}_6\text{H}_5\text{COOH}(aq) + \text{OH}^- (aq) \rightarrow \text{C}_6\text{H}_5\text{COO}^- (aq) + \text{H}_2\text{O}(l)
\begin{array}{c|ccc}
 & C & F & H \\
\hline
S & 1.0 & x & 0 \\
C & x & -x & +x \\
F & 1.0-x & 0 & x \\
\hline
\end{array}
\begin{align*}
4.45 &= 4.20 + \log \left( \frac{x}{1.0-x} \right); \ \text{solve for } x; \ 0.25 = \log \left( \frac{x}{1.0-x} \right); \\
10^{0.25} &= 10 \log \left( \frac{x}{1.0-x} \right); \ 1.778 = \frac{x}{1.0-x}; \ 1.778-1.778x = x; \ 2.778x = 1.778; \ x = 0.64\text{mol NaOH}; \ M = \text{mol/L}; \ \text{solve for } L;
L = \frac{\text{mol}}{M}; \ L = \frac{0.64\text{mol}}{0.50M} = 1.28L \\
\end{align*}
\}

17. 0.24L of 0.75M \text{HCl} \{\text{Part I. Rxn: } \text{NH}_3(aq) + \text{H}_3\text{O}^+(aq) \rightarrow \text{NH}_4^+(aq) + \text{H}_2\text{O}(l) \ \text{do SCF table;}
\begin{array}{c|ccc}
 & S & C & F \\
\hline
\text{NH}_3(aq) + \text{H}_3\text{O}^+(aq) & \text{NH}_4^+(aq) + \text{H}_2\text{O}(l) \\
0.50 & x & 0 & - \\
- & -x & +x & +x \\
0.50-x & 0 & x & - \\
\hline
\end{array}
\begin{align*}
\text{K}_b &= 1.8 \times 10^{-5}; \ \text{pK}_b = 4.74; \ \text{pK}_a = 9.26; \ \text{Part II: use H-H equation: } pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]}; \ 9.50 = 9.26 + \log \left( \frac{0.50-x}{x} \right);
\text{solve for } x; \ 0.24 = \log \left( \frac{0.50-x}{x} \right); \ 10^{0.24} = 10 \log \left( \frac{0.50-x}{x} \right); \ 1.738 = \frac{0.50-x}{x}; \ 1.738x = 0.50 - x; \ 2.738x = 0.50;
\text{x} = 0.183\text{mol HCl}; \ M = \text{mol/L}; \ \text{solve for } L; \ L = \frac{\text{mol}}{M}; \ L = \frac{0.183\text{mol}}{0.75M} = 0.244L \\
\end{align*}
\}
18. I. c  {buffer capacity often refers to the amount of acid or base that can be added to the buffer before the buffer is depleted; this capacity is related to how many moles of acid or base are present in the buffer; solution I has the most moles of weak acid, HNO\textsubscript{2} (0.1L x 1.0M = 0.1mol HNO\textsubscript{2}) and it has the most moles of weak base, NaNO\textsubscript{2} (0.1L x 2.0M = 0.2mol NaNO\textsubscript{2})}

II. e  {the pH of a buffer can be determined from the H-H equation: pH = pK\textsubscript{a} + \log\frac{[\text{base}]}{[\text{acid}]} ; in all cases the pK\textsubscript{a} is the same; also, the ratio of \frac{[\text{base}]}{[\text{acid}]} is the same for all of the solutions, 2 : 1 for \frac{[\text{base}]}{[\text{acid}]} ; hence, the pH is the same}