### 8.4 Acid Base Reactions and Buffers

The following is a summary of the essential knowledge statements from the AP Chemistry CED.

| Strong |  |
| :---: | :--- |
| Acid <br> + | When a strong acid and a strong base are mixed, they react quantitatively in a reaction <br> represented by the following equation. |
| Strong <br> Base | The pH of the resulting solution may be determined from the concentration of excess <br> reagent. |


| Weak <br> Acid $+$ Strong Base | When a weak acid and a strong base are mixed, they react quantitatively in a reaction represented by the following equation. |
| :---: | :---: |
|  | $\mathrm{HA}(a q)+\mathrm{OH}^{-}(a q) \rightarrow \mathrm{A}^{-}(a q)+\mathrm{H}_{2} \mathrm{O}(l)$ |
|  | If the weak acid is in excess, then a buffer solution is formed. The pH can be determined from the equilibrium constant expression $\left(K_{a}\right)$. If the strong base is in excess, then the pH can be determined from the moles of excess hydroxide ion and the total volume of solution. If they are equimolar, then the pH can be determined from the equilibrium represented by the following equation. |
|  | $\mathrm{A}^{-}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftarrows \mathrm{HA}(a q)+\mathrm{OH}^{-}(a q)$ |


| Weak |  |
| :---: | :--- |
| Base <br> + | When a weak base and a strong acid are mixed, they will react quantitatively in a reaction <br> represented by the following equation. <br> Strong <br> Acid |
| $\mathrm{B}(a q)+\mathrm{H}_{3} \mathrm{O}^{+}(a q) \rightarrow \mathrm{HB}^{+}(a q)+\mathrm{H}_{2} \mathrm{O}(l)$ |  |
| determined from the equilibrium constant expression $\left(K_{b}\right)$. If the strong acid is in excess, <br> then the pH can be determined from the moles of excess hydronium ion and the total <br> volume of solution. If they are equimolar, then the pH can be determined from the <br> equilibrium represented by the following equation. |  |
| $\mathrm{HB}^{+}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftarrows \mathrm{B}(a q)+\mathrm{H}_{3} \mathrm{O}^{+}(a q)$ |  |

[^0]When a weak acid and a weak base are mixed, they will react to an equilibrium state whose reaction may be represented by the following equation.

$$
\mathrm{HA}(a q)+\mathrm{B}(a q) \rightleftarrows \mathrm{A}^{-}(a q)+\mathrm{HB}^{+}(a q)
$$

## Strong Acid + Strong Base Experiments

1. A solution is prepared by combining the following.
100.0 mL of $0.10 \mathrm{M} \mathrm{HCl}(\mathrm{aq})$ and 100.0 mL of $0.10 \mathrm{M} \mathrm{NaOH}(a q)$

| Information about the Acid <br> (Before Mixing) |  | Information about the Base <br> (Before Mixing) |  |  |
| ---: | :--- | :--- | :--- | :---: |
| Moles of $\mathrm{H}^{+}$ | Limiting or Excess? | Moles of $\mathrm{OH}^{-}$ | Limiting or Excess? |  |
| $\mathbf{m o l}$ |  | $\mathbf{~ m o l}$ |  |  |


| Combined Solution (After Mixing) |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| Final Volume | $\left[\mathrm{H}^{+}\right]$ | $\left[\mathrm{OH}^{-}\right]$ | pH |  |
| $\mathbf{L}$ |  | $\boldsymbol{M}$ |  |  |

2. A solution is prepared by combining the following.
260.0 mL of $0.10 \mathrm{M} \mathrm{HBr}(\mathrm{aq})$ and 240.0 mL of $0.10 \mathrm{M} \mathrm{KOH}(\mathrm{aq})$

| Information about the Acid <br> (Before Mixing) |  | Information about the Base <br> (Before Mixing) |  |  |
| ---: | :--- | :--- | :--- | :---: |
| Moles of $\mathrm{H}^{+}$ | Limiting or Excess? | Moles of $\mathrm{OH}^{-}$ | Limiting or Excess? |  |
| $\mathbf{m o l}$ |  | $\mathbf{m o l}$ |  |  |

After the reaction $\mathrm{H}^{+}+\mathrm{OH}^{-} \rightarrow \mathrm{H}_{2} \mathrm{O}$ has occurred, $\qquad$ mol of $\qquad$ remains.

| Combined Solution (After Mixing) |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| Final Volume | $\left[\mathrm{H}^{+}\right]$ | $\left[\mathrm{OH}^{-}\right]$ | pH |  |
| $\mathbf{L}$ |  | $\boldsymbol{M}$ |  |  |

3. A solution is prepared by combining the following.
380.0 mL of $0.10 \mathrm{M} \mathrm{HNO}_{3}(\mathrm{aq})$ and 420.0 mL of $0.050 \mathrm{M} \mathrm{Ba}(\mathrm{OH})_{2}(\mathrm{aq})$

| Information about the Acid <br> (Before Mixing) |  | Information about the Base <br> (Before Mixing) |  |  |
| :---: | :---: | :---: | :--- | :---: |
| Moles of $\mathrm{H}^{+}$ | Limiting or Excess? | Moles of $\mathrm{OH}^{-}$ | Limiting or Excess? |  |
| mol |  | $\mathbf{~ m o l}$ |  |  |

After the reaction $\mathrm{H}^{+}+\mathrm{OH}^{-} \rightarrow \mathrm{H}_{2} \mathrm{O}$ has occurred, $\qquad$ mol of $\qquad$ remains.

| Combined Solution (After Mixing) |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| Final Volume | $\left[\mathrm{H}^{+}\right]$ | $\left[\mathrm{OH}^{-}\right]$ | pH |  |
| $\mathbf{L}$ |  | $\boldsymbol{M}$ |  |  |

## Weak Acid + Strong Base Experiment

4. Nitrous acid, $\mathrm{HNO}_{2}$, is a weak acid that ionizes in aqueous solution according to the equation shown below.

$$
\mathrm{HNO}_{2}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftarrows \mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{NO}_{2}^{-}(a q) \quad K_{a}=4.0 \times 10^{-4}
$$

(a) Calculate the pH of $0.20 \mathrm{M} \mathrm{HNO}_{2}(\mathrm{aq})$. A R-I-C-E table is shown below to guide you.

| $\mathbf{R}$ | $\mathrm{HNO}_{2}(a q)$ | + | $\mathrm{H}_{2} \mathrm{O}(l)$ | $\rightleftarrows$ | $\mathrm{H}_{3} \mathrm{O}^{+}(a q)$ | + | $\mathrm{NO}_{2}^{-}(a q)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{I}$ | $\mathbf{0 . 2 0} \boldsymbol{M}$ |  | $\mathbf{N} / \mathbf{A}$ |  | $\approx \mathbf{0} \boldsymbol{M}$ |  | $\mathbf{0} \boldsymbol{M}$ |
| $\mathbf{C}$ |  |  | $\mathbf{N} / \mathbf{A}$ |  |  |  |  |
| $\mathbf{E}$ |  |  | $\mathbf{N} / \mathbf{A}$ |  |  |  |  |

$$
K_{a}=4.0 \times 10^{-4}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{NO}_{2}^{-}\right]}{\left[\mathrm{HNO}_{2}\right]}
$$

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\ldots M
$$

$$
\mathrm{pH}=
$$

$\qquad$

Guidelines for solving a (Weak Acid + Strong Base) problem:

- Make a R-I-C-E table for the reaction between the weak acid HA and $\mathrm{OH}^{-}$. It is often easier to use units of moles in this R-I-C-E table instead of units of $\mathrm{mol} / \mathrm{L}$.
- If moles of $\mathrm{OH}^{-}$are less than the original moles of HA, use the data from the "E" row and the total volume of solution (in L) to calculate [HA] and $\left[\mathrm{A}^{-}\right]$in units of $\mathrm{mol} / \mathrm{L}$. Plug in the values for [HA] and [ $\mathrm{A}^{-}$] into the $K_{a}$ expression. Make assumptions to avoid using the quadratic equation. Solve for $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$. Calculate pH .
- If $\mathrm{OH}^{-}$and HA are equimolar, this means that all the original HA molecules have been converted into $\mathrm{A}^{-}$ions. Switch from $K_{a}$ to $K_{b}$ at this point because of the presence of the conjugate base, $\mathrm{A}^{-}$, which reacts with water as follows: $\mathrm{A}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftarrows \mathrm{HA}+\mathrm{OH}^{-}$
Use the data from the "E" row and the total volume of solution (in L) to calculate [ $A^{-}$] in units of $\mathrm{mol} / \mathrm{L}$. Plug in the value of $\left[\mathrm{A}^{-}\right]$into the $K_{b}$ expression. Solve for $\left[\mathrm{OH}^{-}\right]$. Calculate pOH and pH .
- If moles of $\mathrm{OH}^{-}$are greater than the original moles of HA , there is an excess amount of $\mathrm{OH}^{-}$in solution. Use the data from the "E" row and the total volume of solution (in L) to calculate $\left[\mathrm{OH}^{-}\right]$ in units of $\mathrm{mol} / \mathrm{L}$. Calculate pOH and pH .

4. (continued)
(b) Before the half-equivalence point

| Volume of 0.20 M HNO |  |
| :---: | :---: |
| 2 | $(a q)$ |
| 50.0 mL | Volume of $0.20 \mathrm{M} \mathrm{NaOH}(a q)$ (titrant) |


| $\mathbf{R}$ | $\mathrm{HNO}_{2}(a q)$ | + | $\mathrm{OH}^{-}(a q)$ | $\rightleftarrows$ | $\mathrm{NO}_{2}^{-}(a q)$ | + | $\mathrm{H}_{2} \mathrm{O}(l)$ |
| :---: | ---: | ---: | ---: | ---: | ---: | :---: | :---: |
| $\mathbf{I}$ | $\mathbf{m o l}$ |  | $\mathbf{m o l}$ | $\mathbf{m o l}$ |  | N/A |  |
| $\mathbf{C}$ | $\mathbf{m o l}$ |  | $\mathbf{m o l}$ |  | $\mathbf{m o l}$ |  | N/A |
| $\mathbf{E}$ | $\mathbf{m o l}$ | $\mathbf{m o l}$ | $\mathbf{m o l}$ |  | N/A |  |  |

$\left[\mathrm{HNO}_{2}\right]=$ $\qquad$ M
$\left[\mathrm{NO}_{2}^{-}\right]=$ $\qquad$

$$
K_{a}=4.0 \times 10^{-4}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{NO}_{2}^{-}\right]}{\left[\mathrm{HNO}_{2}\right]}
$$

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\ldots M
$$ $\mathrm{pH}=$ $\qquad$

(c) At the half-equivalence point

| Volume of $0.20 \mathrm{M} \mathrm{HNO}_{2}(a q)$ | Volume of $0.20 \mathrm{M} \mathrm{NaOH}(a q)$ (titrant) |
| :---: | :---: |
| 50.0 mL | 25.0 mL |


| $\mathbf{R}$ | $\mathrm{HNO}_{2}(a q)$ | + | $\mathrm{OH}^{-}(a q)$ | $\rightleftarrows$ | $\mathrm{NO}_{2}^{-}(a q)$ | + | $\mathrm{H}_{2} \mathrm{O}(l)$ |
| :---: | ---: | ---: | ---: | ---: | ---: | :---: | :---: |
| $\mathbf{I}$ | $\mathbf{0 . 0 1 0} \mathbf{~ m o l}$ |  | $\mathbf{m o l}$ | $\mathbf{0 ~ m o l}$ |  | N/A |  |
| $\mathbf{C}$ | $\mathbf{m o l}$ |  | $\mathbf{m o l}$ |  | $\mathbf{m o l}$ |  | N/A |
| $\mathbf{E}$ | $\mathbf{m o l}$ | $\mathbf{m o l}$ | $\mathbf{m o l}$ | N/A |  |  |  |

$$
\left[\mathrm{HNO}_{2}\right]=\ldots M
$$

$\left[\mathrm{NO}_{2}^{-}\right]=$ $\qquad$

$$
K_{a}=4.0 \times 10^{-4}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{NO}_{2}^{-}\right]}{\left[\mathrm{HNO}_{2}\right]}
$$

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\ldots M
$$ $\mathrm{pH}=$ $\qquad$

4. (continued)
(d) Past the half-equivalence point

| Volume of 0.20 M HNO |  |
| :---: | :---: |
| 2 | $(a q)$ |
| 50.0 mL | Volume of $0.20 \mathrm{M} \mathrm{NaOH}(a q)$ (titrant) |


| $\mathbf{R}$ | $\mathrm{HNO}_{2}(a q)$ | + | $\mathrm{OH}^{-}(a q)$ | $\rightleftarrows$ | $\mathrm{NO}_{2}^{-}(a q)$ | + | $\mathrm{H}_{2} \mathrm{O}(l)$ |
| :---: | ---: | ---: | ---: | ---: | ---: | :---: | :---: |
| $\mathbf{I}$ | $\mathbf{0 . 0 1 0} \mathbf{~ m o l}$ |  | $\mathbf{m o l}$ | $\mathbf{0 ~ m o l}$ |  | $\mathbf{N} / \mathbf{A}$ |  |
| $\mathbf{C}$ | $\mathbf{m o l}$ |  | $\mathbf{m o l}$ |  | $\mathbf{m o l}$ |  | N/A |
| $\mathbf{E}$ | $\mathbf{m o l}$ | $\mathbf{m o l}$ | $\mathbf{m o l}$ |  | $\mathbf{N} / \mathbf{A}$ |  |  |

$\left[\mathrm{HNO}_{2}\right]=\ldots M$
$\left[\mathrm{NO}_{2}^{-}\right]=\ldots M$
$K_{a}=4.0 \times 10^{-4}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{NO}_{2}^{-}\right]}{\left[\mathrm{HNO}_{2}\right]}$ $\qquad$
$\mathrm{pH}=$ $\qquad$
(e) At the equivalence point

| Volume of $0.20 \mathrm{M} \mathrm{HNO}_{2}(a q)$ | Volume of $0.20 \mathrm{M} \mathrm{NaOH}(a q)$ (titrant) |
| :---: | :---: |
| 50.0 mL | 50.0 mL |


| $\mathbf{R}$ | $\mathrm{HNO}_{2}(a q)$ | + | $\mathrm{OH}^{-}(a q)$ | $\rightleftarrows$ | $\mathrm{NO}_{2}^{-}(a q)$ | + | $\mathrm{H}_{2} \mathrm{O}(l)$ |
| :---: | ---: | ---: | ---: | ---: | ---: | :---: | :---: |
| $\mathbf{I}$ | $\mathbf{0 . 0 1 0} \mathbf{~ m o l}$ |  | $\mathbf{m o l}$ | $\mathbf{0 ~ m o l}$ |  | N/A |  |
| $\mathbf{C}$ | $\mathbf{m o l}$ |  | $\mathbf{m o l}$ |  | $\mathbf{m o l}$ |  | N/A |
| $\mathbf{E}$ | $\mathbf{m o l}$ | $\mathbf{m o l}$ | $\mathbf{m o l}$ |  | N/A |  |  |

$\left[\mathrm{HNO}_{2}\right]=$ $\qquad$ $\left[\mathrm{NO}_{2}^{-}\right]=$ $\qquad$
Change from $K_{a}$ to $K_{b}$ at this point because $\mathrm{NO}_{2}{ }^{-}$behaves as a weak base in aqueous solution.

$$
\mathrm{NO}_{2}^{-}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftarrows \mathrm{HNO}_{2}(a q)+\mathrm{OH}^{-}(a q)
$$

$K_{a} \times K_{b}=K_{w}=1.0 \times 10^{-14}$
$\left[\mathrm{OH}^{-}\right]=$ $\qquad$ M

$$
\mathrm{pOH}=
$$

$\qquad$

$$
\mathrm{pH}=
$$

$\qquad$
4. (continued)
(f) Past the equivalence point

| Volume of 0.20 M HNO |  |
| :---: | :---: |
| 2 | $(a q)$ |
| 50.0 mL | Volume of $0.20 \mathrm{M} \mathrm{NaOH}(a q)$ (titrant) |


| $\mathbf{R}$ | $\mathrm{HNO}_{2}(a q)$ | + | $\mathrm{OH}^{-}(a q)$ | $\rightleftarrows$ | $\mathrm{NO}_{2}^{-}(a q)$ | + | $\mathrm{H}_{2} \mathrm{O}(l)$ |
| :---: | ---: | ---: | ---: | ---: | ---: | :---: | :---: |
| $\mathbf{I}$ | $\mathbf{0 . 0 1 0} \mathbf{~ m o l}$ |  | $\mathbf{m o l}$ | $\mathbf{0 ~ m o l}$ |  | N/A |  |
| $\mathbf{C}$ | $\mathbf{m o l}$ |  | $\mathbf{m o l}$ |  | $\mathbf{m o l}$ |  | N/A |
| $\mathbf{E}$ | $\mathbf{m o l}$ | $\mathbf{m o l}$ | $\mathbf{m o l}$ |  | N/A |  |  |

$\left[\mathrm{OH}^{-}\right]=$ $\qquad$ M
$\qquad$
$\mathrm{pOH}=$
$\mathrm{pH}=$

## Weak Acid + Strong Base Experiment



| Point | Description | $\mathbf{p H}$ |
| :---: | :---: | :---: |
| A | Initial pH of the weak acid, HA | 2.05 |
| B | Before the half-equivalence point; $[\mathrm{HA}]>\left[\mathrm{A}^{-}\right]$and $\mathrm{pH}<\mathrm{p} K_{a}$ | 3.22 |
| C | At the half-equivalence point; $[\mathrm{HA}]=\left[\mathrm{A}^{-}\right]$and $\mathrm{pH}=\mathrm{p} K_{a}$ | 3.40 |
| D | Past the half-equivalence point; $[\mathrm{HA}]<\left[\mathrm{A}^{-}\right]$and $\mathrm{pH}>\mathrm{p} K_{a}$ | 3.57 |
| E | At the equivalence point; Switch from $K_{a}$ to $K_{b}$ because of the presence of the <br> conjugate base, $\mathrm{A}^{-}$, which reacts with water as follows: $\mathrm{A}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftarrows \mathrm{HA}+\mathrm{OH}^{-}$ | 8.20 |
| F | Past the equivalence point; There is an excess amount of $\mathrm{OH}^{-}$in solution. | 11.98 |

## Weak Base + Strong Acid Experiment

5. Ammonia, $\mathrm{NH}_{3}$, is a weak base that ionizes in aqueous solution according to the equation shown below.

$$
\mathrm{NH}_{3}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftarrows \mathrm{NH}_{4}^{+}(a q)+\mathrm{OH}^{-}(a q) \quad K_{b}=1.8 \times 10^{-5}
$$

(a) Calculate the pH of $0.20 \mathrm{MNH}_{3}(\mathrm{aq})$. A R-I-C-E table is shown below to guide you.

| $\mathbf{R}$ | $\mathrm{NH}_{3}(a q)$ | + | $\mathrm{H}_{2} \mathrm{O}(l)$ | $\rightleftarrows$ | $\mathrm{NH}_{4}{ }^{+}(a q)$ | + | $\mathrm{OH}^{-}(a q)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{I}$ | $\mathbf{0 . 2 0} \boldsymbol{M}$ |  | $\mathbf{N} / \mathbf{A}$ |  | $\mathbf{0} \boldsymbol{M}$ |  | $\approx \mathbf{0} \boldsymbol{M}$ |
| $\mathbf{C}$ |  |  | $\mathbf{N} / \mathbf{A}$ |  |  |  |  |
| $\mathbf{E}$ |  |  | $\mathbf{N} / \mathbf{A}$ |  |  |  |  |

$$
K_{b}=1.8 \times 10^{-5}=\frac{\left[\mathrm{NH}_{4}^{+}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{NH}_{3}\right]}
$$

$\qquad$

$$
\mathrm{pOH}=
$$

$\qquad$

$$
\mathrm{pH}=
$$

$\qquad$

Guidelines for solving a (Weak Base + Strong Acid) problem:

- Make a R-I-C-E table for the reaction between the weak base B and $\mathrm{H}_{3} \mathrm{O}^{+}$. It is often easier to use units of moles in this R-I-C-E table instead of units of $\mathrm{mol} / \mathrm{L}$.
- If moles of $\mathrm{H}_{3} \mathrm{O}^{+}$are less than the original moles of B , use the data from the " E " row and the total volume of solution (in L ) to calculate $[\mathrm{B}]$ and $\left[\mathrm{HB}^{+}\right]$in units of mol/L. Plug in the values for $[\mathrm{B}]$ and $\left[\mathrm{HB}^{+}\right]$into the $K_{b}$ expression. Make assumptions to avoid using the quadratic equation. Solve for $\left[\mathrm{OH}^{-}\right]$. Calculate pOH and pH .
- If $\mathrm{H}_{3} \mathrm{O}^{+}$and B are equimolar, this means that all the original B molecules have been converted into $\mathrm{HB}^{+}$ions. Switch from $K_{b}$ to $K_{a}$ at this point because of the presence of the conjugate acid, $\mathrm{HB}^{+}$, which reacts with water as follows: $\mathrm{HB}^{+}+\mathrm{H}_{2} \mathrm{O} \rightleftarrows \mathrm{B}+\mathrm{H}_{3} \mathrm{O}^{+}$
Use the data from the "E" row and the total volume of solution (in $L$ ) to calculate $\left[\mathrm{HB}^{+}\right]$in units of $\mathrm{mol} / \mathrm{L}$. Plug in the value of $\left[\mathrm{HB}^{+}\right]$into the $K_{a}$ expression. Solve for $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$. Calculate pH .
- If moles of $\mathrm{H}_{3} \mathrm{O}^{+}$are greater than the original moles of B , there is an excess amount of $\mathrm{H}_{3} \mathrm{O}^{+}$in solution. Use the data from the "E" row and the total volume of solution (in L ) to calculate $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$ in units of $\mathrm{mol} / \mathrm{L}$. Calculate pH .

5. (continued)
(b) Before the half-equivalence point

| Volume of $0.20 \mathrm{MNH}_{3}(a q)$ | Volume of $0.20 M \mathrm{HNO}_{3}(a q)$ (titrant) |
| :---: | :---: |
| 50.0 mL | 20.0 mL |


| $\mathbf{R}$ | $\mathrm{NH}_{3}(a q)$ | + | $\mathrm{H}_{3} \mathrm{O}^{+}(a q)$ | $\rightleftarrows$ | $\mathrm{NH}_{4}{ }^{+}(a q)$ | + | $\mathrm{H}_{2} \mathrm{O}(l)$ |
| :---: | ---: | ---: | ---: | ---: | ---: | :---: | :---: |
| $\mathbf{I}$ | $\mathbf{m o l}$ |  | $\mathbf{m o l}$ |  | $\mathbf{m o l}$ |  | N/A |
| $\mathbf{C}$ | $\mathbf{m o l}$ |  | $\mathbf{m o l}$ |  | $\mathbf{m o l}$ |  | N/A |
| $\mathbf{E}$ | $\mathbf{m o l}$ | $\mathbf{m o l}$ |  | $\mathbf{m o l}$ |  | N/A |  |

$\left[\mathrm{NH}_{3}\right]=$ $\qquad$
$\left[\mathrm{NH}_{4}{ }^{+}\right]=$ $\qquad$ M
$K_{b}=1.8 \times 10^{-5}=\frac{\left[\mathrm{NH}_{4}^{+}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{NH}_{3}\right]}$
$\left[\mathrm{OH}^{-}\right]=$ $\qquad$

$$
\mathrm{pOH}=
$$

$\qquad$ $\mathrm{pH}=$ $\qquad$
(c) At the half-equivalence point

| Volume of $0.20 \mathrm{MNH}_{3}(\mathrm{aq})$ | Volume of $0.20 M \mathrm{HNO}_{3}(\mathrm{aq})$ (titrant) |
| :---: | :---: |
| 50.0 mL | 25.0 mL |


| $\mathbf{R}$ | $\mathrm{NH}_{3}(a q)$ | + | $\mathrm{H}_{3} \mathrm{O}^{+}(a q)$ | $\rightleftarrows$ | $\mathrm{NH}_{4}{ }^{+}(a q)$ | + | $\mathrm{H}_{2} \mathrm{O}(l)$ |
| :---: | ---: | ---: | ---: | ---: | ---: | :---: | :---: |
| $\mathbf{I}$ | $\mathbf{0 . 0 1 0} \mathbf{~ m o l}$ |  | $\mathbf{m o l}$ | $\mathbf{0 ~ m o l}$ |  | N/A |  |
| $\mathbf{C}$ | $\mathbf{m o l}$ |  | $\mathbf{m o l}$ |  | $\mathbf{m o l}$ |  | N/A |
| $\mathbf{E}$ | $\mathbf{m o l}$ | $\mathbf{m o l}$ | $\mathbf{m o l}$ |  | N/A |  |  |

$\left[\mathrm{NH}_{3}\right]=$ $\qquad$ M
$\left[\mathrm{NH}_{4}{ }^{+}\right]=$ $\qquad$ M

$$
K_{b}=1.8 \times 10^{-5}=\frac{\left[\mathrm{NH}_{4}^{+}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{NH}_{3}\right]}
$$

$$
\left[\mathrm{OH}^{-}\right]=
$$

$\qquad$ M

$$
\mathrm{pOH}=
$$

$\qquad$

$$
\mathrm{pH}=
$$

$\qquad$
5. (continued)
(d) Past the half-equivalence point

| Volume of $0.20 \mathrm{MNH}_{3}(\mathrm{aq})$ | Volume of $0.20 M \mathrm{HNO}_{3}(\mathrm{aq})$ (titrant) |
| :---: | :---: |
| 50.0 mL | 30.0 mL |


| $\mathbf{R}$ | $\mathrm{NH}_{3}(a q)$ | + | $\mathrm{H}_{3} \mathrm{O}^{+}(a q)$ | $\rightleftarrows$ | $\mathrm{NH}_{4}{ }^{+}(a q)$ | + | $\mathrm{H}_{2} \mathrm{O}(l)$ |
| :---: | ---: | ---: | ---: | ---: | ---: | :---: | :---: |
| $\mathbf{I}$ | $\mathbf{0 . 0 1 0} \mathbf{~ m o l}$ |  | $\mathbf{m o l}$ |  | $\mathbf{0} \mathbf{~ m o l}$ |  | N/A |
| $\mathbf{C}$ | $\mathbf{m o l}$ |  | $\mathbf{m o l}$ |  | $\mathbf{m o l}$ |  | N/A |
| $\mathbf{E}$ | $\mathbf{m o l}$ | $\mathbf{m o l}$ |  | $\mathbf{m o l}$ |  | N/A |  |

$\left[\mathrm{NH}_{3}\right]=\ldots M$
$\left[\mathrm{NH}_{4}{ }^{+}\right]=$ $\qquad$ M
$K_{b}=1.8 \times 10^{-5}=\frac{\left[\mathrm{NH}_{4}^{+}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{NH}_{3}\right]}$
$\left[\mathrm{OH}^{-}\right]=$ $\qquad$

$$
\mathrm{pOH}=
$$

$$
\mathrm{pH}=
$$

$\qquad$
(e) At the equivalence point

| Volume of $0.20 \mathrm{M} \mathrm{H}_{3}(\mathrm{aq})$ | Volume of $0.20 \mathrm{M} \mathrm{HNO}_{3}(\mathrm{aq})$ (titrant) |
| :---: | :---: |
| 50.0 mL | 50.0 mL |


| $\mathbf{R}$ | $\mathrm{NH}_{3}(a q)$ | + | $\mathrm{H}_{3} \mathrm{O}^{+}(a q)$ | $\rightleftarrows$ | $\mathrm{NH}_{4}{ }^{+}(a q)$ | + | $\mathrm{H}_{2} \mathrm{O}(l)$ |
| :---: | ---: | ---: | ---: | ---: | ---: | :---: | :---: |
| $\mathbf{I}$ | $\mathbf{0 . 0 1 0} \mathbf{~ m o l}$ |  | $\mathbf{m o l}$ | $\mathbf{0 ~ m o l}$ |  | N/A |  |
| $\mathbf{C}$ | $\mathbf{m o l}$ |  | $\mathbf{m o l}$ |  | $\mathbf{m o l}$ |  | N/A |
| $\mathbf{E}$ | $\mathbf{m o l}$ | $\mathbf{m o l}$ | $\mathbf{m o l}$ |  | N/A |  |  |

$\left[\mathrm{NH}_{3}\right]=$ $\qquad$ M
$\left[\mathrm{NH}_{4}{ }^{+}\right]=$ $\qquad$ M

Change from $K_{b}$ to $K_{a}$ at this point because $\mathrm{NH}_{4}{ }^{+}$behaves as a weak acid in aqueous solution.

$$
\mathrm{NH}_{4}^{+}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftarrows \mathrm{NH}_{3}(a q)+\mathrm{H}_{3} \mathrm{O}^{+}(a q)
$$

$K_{a} \times K_{b}=K_{w}=1.0 \times 10^{-14}$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=$ $\qquad$ M
$\qquad$
5. (continued)
(f) Past the equivalence point

| Volume of $0.20 \mathrm{MNH}_{3}(\mathrm{aq})$ | Volume of $0.20 M \mathrm{HNO}_{3}(\mathrm{aq})$ (titrant) |
| :---: | :---: |
| 50.0 mL | 55.0 mL |


| $\mathbf{R}$ | $\mathrm{NH}_{3}(a q)$ | + | $\mathrm{H}_{3} \mathrm{O}^{+}(a q)$ | $\rightleftarrows$ | $\mathrm{NH}_{4}{ }^{+}(a q)$ | + | $\mathrm{H}_{2} \mathrm{O}(l)$ |
| ---: | ---: | ---: | ---: | ---: | ---: | :---: | :---: |
| $\mathbf{I}$ | $\mathbf{0 . 0 1 0} \mathbf{~ m o l}$ |  | $\mathbf{m o l}$ | $\mathbf{0 ~ m o l}$ |  | N/A |  |
| $\mathbf{C}$ | $\mathbf{m o l}$ |  | $\mathbf{m o l}$ | $\mathbf{m o l}$ |  | N/A |  |
| $\mathbf{E}$ | $\mathbf{m o l}$ | $\mathbf{m o l}$ |  | $\mathbf{m o l}$ |  | N/A |  |

$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=$ $\qquad$

$$
\mathrm{pH}=
$$

$\qquad$

## Weak Base + Strong Acid Experiment



| Point | Description | $\mathbf{p H}$ |
| :---: | :---: | :---: |
| A | Initial pH of the weak base, B | 11.28 |
| B | Before the half-equivalence point; $\left[\mathrm{HB}^{+}\right]<[\mathrm{B}]$ and $\mathrm{pH}>\mathrm{p} K_{a}$ for $\mathrm{HB}^{+}$ | 9.43 |
| C | At the half-equivalence point; $\left[\mathrm{HB}^{+}\right]=[\mathrm{B}]$ and $\mathrm{pH}=\mathrm{p} K_{a}$ for $\mathrm{HB}^{+}$ | 9.26 |
| D | Past the half-equivalence point; $\left[\mathrm{HB}^{+}\right]>[\mathrm{B}]$ and $\mathrm{pH}<\mathrm{p} K_{a}$ for $\mathrm{HB}^{+}$ | 9.08 |
| E | At the equivalence point; Switch from $K_{b}$ to $K_{a}$ because of the presence of the <br> conjugate acid, $\mathrm{HB}^{+}$, which reacts with water as follows: $\mathrm{HB}^{+}+\mathrm{H}_{2} \mathrm{O} \rightleftarrows \mathrm{B}+\mathrm{H}_{3} \mathrm{O}^{+}$ | 5.12 |
| F | Past the equivalence point; There is an excess amount of $\mathrm{H}_{3} \mathrm{O}^{+}$in solution. | 2.02 |

## Weak Acid + Weak Base Experiment

6. Hypochlorous acid, HOCl , is a weak acid. Methylamine, $\mathrm{CH}_{3} \mathrm{NH}_{2}$, is a weak base.
(a) Write the balanced chemical equation for the ionization of HOCl in aqueous solution.
$\square$
(b) Write the balanced chemical equation for the ionization of $\mathrm{CH}_{3} \mathrm{NH}_{2}$ in aqueous solution.
$\square$
(c) Fill in the missing information in the table below.

| Acid | $K_{a}$ | Base | $K_{b}$ |
| :---: | :---: | :---: | :---: |
| HOCl | $3.0 \times 10^{-8}$ | $\mathrm{OCl}^{-}$ |  |
| $\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}$ |  | $\mathrm{CH}_{3} \mathrm{NH}_{2}$ | $4.4 \times 10^{-4}$ |

(d) Write the balanced chemical equation for the acid-base reaction that occurs when solutions of $\mathrm{HOCl}(a q)$ and $\mathrm{CH}_{3} \mathrm{NH}_{2}(a q)$ are combined.
(e) A student mixed 50.0 mL of $0.10 \mathrm{MHOCl}(a q)$ with 50.0 mL of $0.10 M \mathrm{CH}_{3} \mathrm{NH}_{2}(a q)$. Is the resulting solution acidic, basic, or neutral? Justify your answer in terms of the relative values of $K_{a}$ and $K_{b}$ for the products of the reaction represented by the equation you wrote in part (d).

### 8.5 Acid Base Titrations

Essential knowledge statements from the AP Chemistry CED:

- An acid-base reaction can be carried out under controlled conditions in a titration. A titration curve, plotting pH against the volume of titrant added, is useful for summarizing results from a titration.
- At the equivalence point, the number of moles of titrant added is equal to the number of moles of analyte originally present. This relationship can be used to obtain the concentration of the analyte. This is the case for titrations of strong acids/bases and weak acids/bases.
- For titrations of weak acids/bases, it is useful to consider the point halfway to the equivalence point, that is, the half-equivalence point. At this point, there are equal concentrations of each species in the conjugate acid-base pair. For example, for a weak acid [HA] $=\left[\mathrm{A}^{-}\right]$. Because $\mathrm{pH}=\mathrm{p} K_{a}$ when the conjugate acid and base have equal concentrations, the $\mathrm{p} K_{a}$ can be determined from the pH at the half-equivalence point in a titration.
- For polyprotic acids, titration curves can be used to determine the number of acidic protons. In doing so, the major species present at any point along the curve can be identified, along with the $\mathrm{p} K_{\mathrm{a}}$ associated with each proton in a weak polyprotic acid.


### 4.6 Introduction to Titration (Review)

Essential knowledge statement from the AP Chemistry CED:

- Titrations may be used to determine the concentration of an analyte in solution. The titrant has a known concentration of a species that reacts specifically and quantitatively with the analyte. The equivalence point of the titration occurs when the analyte is totally consumed by the reacting species in the titrant. The equivalence point is often indicated by a change in a property (such as color) that occurs when the equivalence point is reached. This observable event is called the endpoint of the titration.


7. A student is given a sample of $\mathrm{HCl}(a q)$ of unknown concentration. The student performs a titration experiment to determine the concentration of HCl in the solution.
8. (continued)

(a) The student titrates a 20.0 mL sample of the HCl solution with $0.180 \mathrm{M} \mathrm{NaOH}(a q)$. Based on the titration curve above, what is the molar concentration of HCl in the solution?
(b) Accurately sketch the curve on the graph below to represent the expected titration curve if the student titrates a 10.0 mL sample of the HCl solution with $0.180 \mathrm{M} \mathrm{NaOH}(a q)$.


Volume of 0.180 M NaOH Added ( mL )
(c) Accurately sketch the curve on the graph below to represent the expected titration curve if the student titrates a 40.0 mL sample of the HCl solution with $0.180 \mathrm{M} \mathrm{NaOH}(a q)$.


Volume of 0.180 M NaOH Added (mL)
8. A student is given a sample of formic acid, $\mathrm{HCO}_{2} \mathrm{H}$. The student performs a titration experiment to determine the concentration of $\mathrm{HCO}_{2} \mathrm{H}$ in the solution.

(a) The student titrates a 50.0 mL sample of the $\mathrm{HCO}_{2} \mathrm{H}$ solution with $0.20 \mathrm{M} \mathrm{NaOH}(a q)$. Based on the titration curve above, the concentration of $\mathrm{HCO}_{2} \mathrm{H}$ in the solution is $\qquad$ $\mathrm{mol} / \mathrm{L}$
(b) After 12.5 mL of the titrant has been added, the pH of the reaction mixture is equal to 3.75 . Use this information to calculate the value of $K_{a}$ for $\mathrm{HCO}_{2} \mathrm{H}$.

$$
K_{a}=
$$

$\qquad$
(c) Accurately sketch the curve on the graph below to represent the expected titration curve if the student titrates a 50.0 mL sample of $0.10 M \mathrm{HCO}_{2} \mathrm{H}(\mathrm{aq})$ with $0.10 \mathrm{M} \mathrm{NaOH}(\mathrm{aq})$.

(d) Accurately sketch the curve on the graph below to represent the expected titration curve if the student titrates a 50.0 mL sample of $0.10 \mathrm{M} \mathrm{HCO}_{2} \mathrm{H}(a q)$ with $0.40 \mathrm{M} \mathrm{NaOH}(a q)$.

9. Information about two different titration experiments is shown above, along with the titration curve for each experiment.
(a) When the equivalence point is reached in experiment \#1, the pH is equal to 7.0. Circle all of the substances listed below that are present in the reaction mixture at a concentration greater than 0.01 M at the equivalence point.
$\mathrm{H}_{3} \mathrm{O}^{+}$
$\mathrm{Cl}^{-}$
$\mathrm{Na}^{+}$
$\mathrm{OH}^{-}$
(b) When the equivalence point is reached in experiment \#2, the pH is equal to 7.0 . Circle all of the substances listed below that are present in the reaction mixture at a concentration greater than 0.01 M at the equivalence point.
$\mathrm{H}_{3} \mathrm{O}^{+}$
$\mathrm{NO}_{3}{ }^{-}$
$\mathrm{K}^{+}$
$\mathrm{OH}^{-}$
(c) Based on your answers to parts (a) and (b), explain why the pH is equal to 7.0 at the equivalence point in each of these titration experiments.

10. The titration curves for two different titration experiments are shown above.
(a) Fill in the missing information in the table below.

|  | Experiment \#1 <br> Titration of $\mathrm{HNO}_{3}$ | Experiment \#2 <br> Titration of $\mathrm{HNO}_{2}$ |
| :---: | :---: | :---: |
| Strong Acid or Weak Acid? |  |  |
| Initial pH of $0.10 \mathrm{MHA}(\mathrm{aq})$ |  | 2.21 |
| pH at the half-equivalence point | 1.48 | 3.41 |
| pH at the equivalence point |  | 8.05 |

(b) Use the information from the titration curve for Experiment \#2 to calculate each of the following.
$\mathrm{p} K_{a}$ for $\mathrm{HNO}_{2}=$ $\qquad$ $K_{a}$ for $\mathrm{HNO}_{2}=$ $\qquad$
(c) When the equivalence point is reached in experiment $\# 2$, the pH is greater than 7.0. Circle all of the substances listed below that are present in the reaction mixture at a concentration greater than 0.01 M at the equivalence point.
$\mathrm{H}_{3} \mathrm{O}^{+}$
$\mathrm{NO}_{2}{ }^{-}$
$\mathrm{Na}^{+}$
$\mathrm{OH}^{-}$
(d) Write the net ionic equation for the acid-base reaction that takes place between one of the ions that you circled in part (c) and $\mathrm{H}_{2} \mathrm{O}(l)$. This reaction should provide evidence to explain why the pH is greater than 7 at the equivalence point in experiment $\# 2$.

11. The titration curves for two different titration experiments are shown above.
(a) Fill in the missing information in the table below.

|  | Experiment \#1 <br> Titration of $\mathrm{HC}_{3} \mathrm{H}_{5} \mathrm{O}_{2}$ | Experiment \#2 <br> Titration of HOCl |
| :---: | :---: | :---: |
| Initial pH of $0.10 \mathrm{MHA}(\mathrm{aq})$ | 2.95 | 4.26 |
| pH at the half-equivalence point | 4.89 | 7.52 |
| $K_{a}$ value for the acid |  |  |
| pH at the equivalence point |  |  |

(b) For each experiment, write the net ionic equation for the acid-base reaction that occurs in the reaction mixture that helps to explain why the pH is greater than 7 at the equivalence point.

| Experiment \#1 | Experiment \#2 |
| :--- | :--- |
|  |  |

(c) Comparing these two titration curves, we can see that the pH at the equivalence point in the HOCl titration is higher than the pH at the equivalence point for the $\mathrm{HC}_{3} \mathrm{H}_{5} \mathrm{O}_{2}$ titration.
This observation can be explained because
HOCl is a ( weaker stronger ) acid than $\mathrm{HC}_{3} \mathrm{H}_{5} \mathrm{O}_{2}$, and the
$\mathrm{OCl}^{-}$ion is a ( weaker stronger ) base than the $\mathrm{C}_{3} \mathrm{H}_{5} \mathrm{O}_{2}^{-}$ion.

| Acid | $\mathrm{p} K_{a}$ | $K_{a}$ |
| :---: | :---: | :---: |
| $\mathrm{HClO}_{2}$ | 2.0 | $1 \times 10^{-2}$ |
| $\mathrm{HClO}_{3}$ | -2.7 | $5 \times 10^{2}$ |

12. Information about $\mathrm{HClO}_{2}$ and $\mathrm{HClO}_{3}$ is listed in the table above.
(a) Which acid is the stronger acid? Justify your answer.

| Experiment \#1 | Experiment \#2 |
| :---: | :---: |
| 50.0 mL of $0.10 M \mathrm{HClO}_{2}$ | 50.0 mL of 0.10 MHClO |
| 3 |  |

(b) The details of two titration experiments are shown above. Which titration experiment will result in a reaction mixture that has a higher pH at the equivalence point? Justify your answer by comparing the relative strengths of the conjugate base for each acid.
(c) A student makes the claim that, when equal volumes of $0.10 M \mathrm{HClO}_{2}(a q)$ and $0.10 \mathrm{M} \mathrm{HClO}_{3}(a q)$ are each titrated with $0.10 \mathrm{M} \mathrm{NaOH}(a q)$, the $\mathrm{HClO}_{3}$ solution should require a greater volume of $\mathrm{NaOH}(a q)$ to reach the equivalence point.
Do you agree or disagree with the student's claim? Justify your answer.


$$
\begin{array}{lll}
\mathrm{H}_{2} \mathrm{SO}_{3}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftarrows \mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{HSO}_{3}^{-} & K_{a 1}=1.4 \times 10^{-2} \\
\mathrm{HSO}_{3}^{-}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftarrows \mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{SO}_{3}{ }^{2-} & K_{a 2}=6.7 \times 10^{-8}
\end{array}
$$

13. Sulfurous acid, $\mathrm{H}_{2} \mathrm{SO}_{3}$ is classified as a diprotic acid. The titration curve shown above is from an experiment in which 25.0 mL of $0.10 \mathrm{MH}_{2} \mathrm{SO}_{3}(a q)$ is titrated with $0.10 \mathrm{M} \mathrm{NaOH}(a q)$.

Fill in the missing information in the table below.

| Point | pH | Substance(s) Present in Solution <br> at the Highest Concentration |
| :---: | :---: | :---: |
| A | 1.51 |  |
| B | 2.08 | Equal amounts of $\mathrm{H}_{2} \mathrm{SO}_{3}$ and $\mathrm{HSO}_{3}{ }^{-}$ |
| C | 4.57 |  |
| D | 7.17 | Equal amounts of $\mathrm{HSO}_{3}{ }^{-}$and $\mathrm{SO}_{3}{ }^{2-}$ |
| E | 9.85 |  |

A titration experiment is performed in which a sample of a weak acid, $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\left(\mathrm{p} K_{a}=4.74\right)$ is titrated with NaOH . The titration curve is shown at right. The particle diagrams shown below display representative samples of the reaction mixture at points A through F in the titration.



| Point A <br> Sample of the weak acid, HA | Point B <br> Before half-equivalence point; <br> $[\mathrm{HA}]>\left[\mathrm{A}^{-}\right]$and $\mathrm{pH}<\mathrm{p} K_{a}$ | Point C <br> Half-equivalence point; $[\mathrm{HA}]=\left[\mathrm{A}^{-}\right]$and $\mathrm{pH}=\mathrm{p} K_{a}$ |
| :---: | :---: | :---: |
|  |  |  |
| Point D <br> Past the half-equivalence point; <br> $[\mathrm{HA}]<\left[\mathrm{A}^{-}\right]$and $\mathrm{pH}>\mathrm{p} K_{a}$ | ```Point E Equivalence point; \(\mathrm{pH}>7\) because of this reaction: \[ \mathrm{A}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftarrows \mathrm{HA}+\mathrm{OH}^{-} \]``` | Point F <br> Past the equivalence point; Excess amount of $\mathrm{OH}^{-}$ions |
|  |  |  |

A titration experiment is performed in which a sample of a weak base, $\mathrm{NH}_{3}\left(\mathrm{p} K_{b}\right.$ for $\mathrm{NH}_{3}=4.74$ and $\mathrm{p} K_{a}$ for $\mathrm{NH}_{4}{ }^{+}=9.25$ ) is titrated with HCl . The titration curve is shown at right.
The particle diagrams shown below display representative samples of the reaction mixture at points A through F in the titration.



| Point A <br> Sample of the weak base, B | Point B <br> Before half-equivalence point; $\begin{gathered} {\left[\mathrm{HB}^{+}\right]<[\mathrm{B}] \text { and }} \\ \mathrm{pH}>\mathrm{p} K_{a} \text { for } \mathrm{HB}^{+} \end{gathered}$ | Point C <br> Half-equivalence point; $\left[\mathrm{HB}^{+}\right]=[\mathrm{B}]$ and $\mathrm{pH}=\mathrm{p} K_{a}$ for $\mathrm{HB}^{+}$ |
| :---: | :---: | :---: |
|  | 880 <br> 80 80 <br> 808 | $8 \% 80$ <br> 80080 <br> $\Rightarrow \quad 80$ |
| Point D <br> Past the half-equivalence point; $\left[\mathrm{HB}^{+}\right]>[\mathrm{B}]$ and $\mathrm{pH}<\mathrm{pK}_{a}$ for $\mathrm{HB}^{+}$ | Point $E$ <br> Equivalence point; $\mathrm{pH}<7$ because of this reaction: $\mathrm{HB}^{+}+\mathrm{H}_{2} \mathrm{O} \rightleftarrows \mathrm{~B}+\mathrm{H}_{3} \mathrm{O}^{+}$ | Point F <br> Past the equivalence point; Excess amount of $\mathrm{H}_{3} \mathrm{O}^{+}$ions |
|  |  |  |


[^0]:    Weak

