## Unit 6: ACIDS AND BASES

## Chapter 16: Acids and Bases

## 16.1: Bronsted Acids and Bases

## Physical and Chemical Properties of Acid and Base

Acids
Taste Sour (Citric Acids).
Burning Sensation (Stomach Acid).
Corrosive with Metals (reacts to give off $\mathrm{H}_{2}(\mathrm{~g})$ ).
Red litmus remains Red; Blue litmus turns Red.
Bromothymol Blue turns Yellow
Phenolphthalein turns Colourless.
pH $<7$
pH Scale


Conceptual Definition: - an explanation that attempts to describe why things are the way they are.
Arrhenius Concept: - acids are $\mathbf{H}^{+}$(proton) producers and bases are $\mathbf{O H}^{-}$producers.
Examples: $\quad \mathrm{HCl}_{(a q)} \rightarrow \mathrm{H}_{(a q)}^{+}+\mathrm{Cl}_{(a q)}^{-} \quad\left(\mathrm{HCl}_{(a q)}\right.$ is an Arrhenius Acid.)

$$
\mathrm{NaOH}_{(a q)} \rightarrow \mathrm{Na}_{(a q)}^{+}+\mathbf{O H}_{(a q)}^{-} \quad\left(\mathrm{NaOH}_{(a q)}\right. \text { is an Arrhenius Base.) }
$$

Bronsted-Lowry Model: - acids and bases react with water to dissociate where acids are $\mathrm{H}^{+}$(proton) donors and bases are $\mathbf{H}^{+}$(proton) acceptors.

- first proposed by Johannes Brønsted and Thomas Lowry.

Hydronium Ion: - an ion formed when an acidd "donated" $\mathrm{H}^{+}$ion combined with a $\mathrm{H}_{2} \mathrm{O}$ molecule to form a $\mathrm{H}_{3} \mathrm{O}^{+}$ion (hydronium ion).

- essentially has the same function as a $\mathrm{H}^{+}$ion, but $\mathrm{H}_{3} \mathrm{O}^{+}$denotes that we are using the Brønsted-Lowry model.

Examples:

$$
\mathrm{HBr}_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{(l)} \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}{ }_{(a q)}+\mathrm{Br}^{-}{ }_{(a q)}
$$

( HBr is a $\mathrm{Br} \varnothing$ nsted-Lowry Acid - donated a proton)
( $\mathrm{H}_{2} \mathrm{O}$ is a Brønsted-Lowry Base - accepted a proton.)
$\mathrm{NH}_{3(a q)}+\mathrm{H}_{2} \mathrm{O}_{(l)} \rightleftharpoons \mathrm{NH}_{4}^{+}{ }_{(a q)}+\mathbf{O H}_{(a q)}^{-}$
( $\mathrm{H}_{2} \mathrm{O}$ is a Brønsted-Lowry Acid - donated a proton)
$\left(\mathrm{NH}_{3}\right.$ is a Brønsted-Lowry Base - accepted a proton.)

Conjugate Base: - the product formed after the Acid donated a $\mathrm{H}^{+} . \quad$ (Acid $\rightarrow$ Conjugate Base) - behaves like a base when the reaction is looking from reverse.

Conjugate Acid: - the product formed after the Base accepted a $\mathrm{H}^{+} . \quad$ (Base $\rightarrow$ Conjugate Acid)

- behaves like a acid when the reaction is looking from reverse.

Conjugate Acid-Base Pair: - the (acid/conjugate base) or (base/conjugate acid) pairs.


## Conjugate Acid-Base Pairs: $\mathrm{B} / \mathrm{HB}^{+}$and $\mathrm{H}_{2} \mathrm{O} / \mathrm{OH}^{-}$

Acid Dissociation Constant ( $\boldsymbol{K}_{\boldsymbol{a}}$ ): - the equilibrium constant of a Brønsted-Lowry Acid Dissociation.
Base Dissociation Constant ( $\boldsymbol{K}_{\boldsymbol{b}}$ ): - the equilibrium constant of a Brønsted-Lowry Base Dissociation.

$$
\begin{array}{cc}
\text { Brønsted-Lowry Acid Dissociation } & \\
\mathbf{H A}_{(a q)}+\mathbf{H}_{2} \mathbf{O}_{(I)} \rightleftharpoons \mathbf{H}_{3} \mathbf{O}_{(a q)}^{+}+{\mathbf{A}_{(a q)}^{-}}^{\text {Bronsted-Lowry Base Dissociation }} \\
K_{a}=\frac{\left[\mathbf{H}_{3} \mathbf{O}^{+} \mathbf{I A}^{-}\right]}{[\mathbf{H A}]} & \mathbf{B}_{(a q)}+\mathbf{H}_{2} \mathbf{O}_{(l)} \rightleftharpoons \mathbf{H B}^{+}{ }_{(a q)}+\mathbf{O H}_{(a q)}^{-} \\
& K_{b}=\frac{\left[\mathbf{H B}^{+} \mathbf{I} \mathbf{O H}^{-}\right]}{[\mathbf{B}]}
\end{array}
$$

Example 1: Write the Brønsted-Lowry dissociation reaction of the following. Identify the Brønsted-Lowry acid and base, along with the conjugate acid and base. Determine the conjugate acid-base pairs. State the equilibrium expression of the dissociation reaction.
a. Acetic acid $\left(\mathrm{CH}_{3} \mathrm{COOH}_{(a q)}\right)$

Conjugate Acid-Base Pairs:
$\mathrm{CH}_{3} \mathrm{COOH} / \mathrm{CH}_{3} \mathrm{COO}^{-}$and $\mathrm{H}_{2} \mathrm{O} / \mathrm{H}_{3} \mathrm{O}^{+}$

$$
K_{a}=\frac{\left[\mathrm{H}_{3} \mathbf{O}^{+} \backslash \mathrm{CH}_{3} \mathrm{COO}^{-}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}
$$

b. Cyanide Ion $\left(\mathrm{CN}^{-}{ }_{(a q)}\right)$
$\mathrm{CN}^{-}{ }_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{(l)} \rightleftharpoons \mathrm{HCN}_{(a q)}+\mathrm{OH}^{-}(a q)$
(Base) (Acid) (Conjugate (Conjugate Acid) Base)

Conjugate Acid-Base Pairs: $\mathrm{CN}^{-} / \mathrm{HCN}$ and $\mathrm{H}_{2} \mathrm{O} / \mathrm{OH}^{-}$

$$
K_{b}=\frac{[\mathrm{HCN}]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{CN}^{-}\right]}
$$

## Assignment

16.1 pg. 568 \#1 to 8

## 16.2: The Acid-Base Properties of Water

Autoionization of Water: - the process where water dissociates into hydronium and hydroxide ions.

- water's dissociation constant is called ion-product constant ( $\left.K_{w}=\mathbf{1 . 0} \times \mathbf{1 0}^{\mathbf{- 1 4}}\right)$ - when the solution is neutral $(\mathrm{pH}=7),\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-7} \mathrm{~mol} / \mathrm{L}$

$$
\begin{gathered}
\text { Autoionization of Water } \\
2 \mathrm{H}_{2} \mathrm{O}_{(l)} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}_{(a q)}^{+}+\mathrm{OH}_{(a q)}^{-} \\
K_{w}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14} \text { at } 25^{\circ} \mathrm{C} \\
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{K_{w}}{\left[\mathrm{OH}^{-}\right] \quad\left[\mathrm{OH}^{-}\right]=\frac{K_{w}}{\left[\mathbf{H}_{3} \mathbf{O}^{+}\right]}}} \\
\text {At } \mathrm{pH}=7:\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-7} \mathrm{~mol} / \mathrm{L}
\end{gathered}
$$

Example 1: At $25^{\circ} \mathrm{C}, K_{w}=1.0 \times 10^{-14}$.
a. Using the ICE box, show that $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-7} \mathrm{~mol} / \mathrm{L}$ for a neutral solution.
b. At $100^{\circ} \mathrm{C}, K_{w}=8.19 \times 10^{-13}$. What is the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$and $\left[\mathrm{OH}^{-}\right]$for a neutral solution at $100^{\circ} \mathrm{C}$ ?
a. $\quad 2 \mathbf{H}_{2} \mathrm{O}_{(I)} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}_{(a q)}+\mathbf{O H}_{(a q)}^{-}$

|  | $\mathbf{H}_{2} \mathbf{O}_{(I)}$ | $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$ | $\left[\mathrm{OH}^{-}\right]$ |  |
| :--- | :---: | :---: | :---: | :---: |
| Initial | ---- | 0 | $\begin{array}{c}0 \\ \text { Change }\end{array}$ | ---- |
| $+\boldsymbol{x}$ |  |  |  |  |$]$

$$
K_{w}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]
$$

$$
1.0 \times 10^{-14}=(x)(x)
$$

$$
x^{2}=\sqrt{1.0 \times 10^{-14}}
$$

$$
x=1.0 \times 10^{-7}
$$

$$
x=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-7} \mathrm{M}
$$

b. At $100^{\circ} \mathrm{C}$, using $K_{w}=8.19 \times 10^{-13}$

$$
\begin{array}{rlr}
K_{w} & =\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right] & x=2.86 \times 10^{-7} \\
8.19 \times 10^{-13} & =(x)(x) & \\
x^{2} & =\sqrt{8.19 \times 10^{-13}} & x=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left[\mathbf{O H}^{-}\right]=\mathbf{2 . 8 6} \times \mathbf{1 0}^{-7} \mathbf{M}
\end{array}
$$

Example 2: Determine the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$and/or $\left[\mathrm{OH}^{-}\right]$concentrations of the following solutions at $25^{\circ} \mathrm{C}$.
a. $\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-4} \mathrm{~mol} / \mathrm{L}$
$K_{w}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{K_{w}}{\left[\mathrm{OH}^{-}\right]}=\frac{1.0 \times 10^{-14}}{1.0 \times 10^{-4}}$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1.0 \times 10^{-10} \mathrm{~mol} / \mathrm{L}$
b. $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=5.0 \times 10^{-5} \mathrm{M}$
$K_{w}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]$
$\left[\mathrm{OH}^{-}\right]=\frac{K_{w}}{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}=\frac{1.0 \times 10^{-14}}{5.0 \times 10^{-5}}$
$\left[\mathrm{OH}^{-}\right]=2.0 \times 10^{-10} \mathrm{M}$

## 16.3: pH - A Measure of Acidity

pH Scale: - a logarithmic scale to measure the acidity (relative $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$) of a solution.

- the lower the pH , the more acidic (less basic) is the solution (more $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$and less $\left[\mathrm{OH}^{-}\right]$).
- the higher the $\mathbf{p H}$, the more basic (less acidic) is the solution (less $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$and more $\left[\mathrm{OH}^{-}\right]$).
- acidity is NOT the same as the acid strength. Just because a solution has a low pH , it does not mean that it is a strong acid. (Highly Acidic $\neq$ Strong Acid)
- it is normally reported between 0 to 14 (with 7 as neutral), but it can be above 14 (very basic) or below 0 (very acidic).
- an increase of 1 on a pH scale means a decrease of $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$by a factor of 10 ; an increase of 2 on a pH scale means a decrease of $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$by a factor of $\mathbf{1 0 0}$.


Example: pH of Some Common Substances

| Substance | $\mathbf{p H}$ |
| :--- | :--- |
| 1 M of HCl | 0.00 |
| Stomach Acid | 2.00 |
| Lemon Juice | 2.50 |
| Vinegar | 3.00 |


| Substance | pH |
| :--- | :--- |
| Milk | 6.30 |
| Rain Water | 6.70 |
| Pure Water | 7.00 |
| Blood | 7.50 |


| Substance | $\mathbf{p H}$ |
| :--- | :---: |
| 1 M of Baking Soda $\left(\mathrm{NaHCO}_{3}\right)$ | 9.68 |
| Ammonia as Household Cleaner | 12.00 |
| 1 M of NaOH | 14.00 |

pOH Scale: - a logarithmic scale to measure the basicity (relative [ $\left.\mathrm{OH}^{-}\right]$) of a solution.

- the lower the $\mathbf{p O H}$, the more basic (less acidic) is the solution (more $\left[\mathrm{OH}^{-}\right]$and less $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$).
- the higher the $\mathbf{p O H}$, the less basic (more acidic) is the solution (less $\left[\mathrm{OH}^{-}\right]$and more $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$).
- basicity is NOT the same as the base strength. Just because a solution has a low pOH, it does not mean that it is a strong base. (Highly Basic $\neq$ Strong Base)
- it is normally reported between 0 to 14 (with 7 as neutral), but it can be above 14 (very acidic) or below 0 (very basic).
- an increase of 1 on a pOH scale means a decrease of $\left[\mathrm{OH}^{-}\right]$by a factor of 10 ; an increase of 2 on a $\mathbf{p O H}$ scale means a decrease of $\left[\mathrm{OH}^{-}\right]$by a factor of $\mathbf{1 0 0}$.


$$
\frac{\mathrm{pH} \text { and pOH Scales }}{\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \quad \mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right]} \text {pH+pOH=14.00}
$$

Example 1: Calculate the pH and the pOH for the following solutions.
a. $0.0100 \mathrm{~mol} / \mathrm{L}$ of $\mathrm{HI}_{(a q)}$ (completely dissociates) b. $5.00 \times 10^{-6} \mathrm{M}$ of $\mathrm{HClO}_{4 \text { (aq) }}$ (completely dissociates)

$$
\mathrm{HI}_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{(l)} \rightarrow \mathrm{H}_{3} \mathrm{O}_{(a q)}^{+}+\mathrm{I}_{(a q)}^{-}
$$

(Strong Acid: $\left.[\mathrm{HI}]_{0}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=0.0100 \mathrm{M}\right)$

$$
\begin{array}{rl}
\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right] & \mathrm{pOH}=14-\mathrm{pH} \\
\mathrm{pH}=-\log (0.0100) & \mathrm{pOH}=14-2.00 \\
\mathrm{pH}=\mathbf{2 . 0 0} & \mathbf{p O H}=\mathbf{1 2 . 0 0}
\end{array}
$$

c. 1.50 M of $\mathrm{KOH}_{(a q)}$

$$
\mathrm{KOH}_{(a q)} \rightarrow \mathrm{K}_{(a q)}^{+}+\mathrm{OH}_{(a q)}^{-}
$$

(Ionic Strong Base: $\left.[\mathrm{KOH}]_{0}=\left[\mathrm{OH}^{-}\right]=\mathbf{1 . 5 0} \mathrm{M}\right)$

$$
\mathrm{HClO}_{4(a q)}+\mathrm{H}_{2} \mathrm{O}_{(l)} \rightarrow \mathrm{H}_{3} \mathrm{O}_{(a q)}^{+}+\mathrm{ClO}_{4}^{-}{ }_{(a q)}
$$

$$
\text { (Strong Acid: } \left.\left[\mathrm{HClO}_{4}\right]_{0}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=5.00 \times 10^{-6} \mathbf{M}\right)
$$

$$
\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \quad \mathrm{pOH}=14-\mathrm{pH}
$$

$$
\mathrm{pH}=-\log \left(5.00 \times 10^{-6}\right)
$$

$$
\mathrm{pOH}=14-5.30
$$

$\mathrm{pH}=5.30$
$\mathrm{pOH}=8.70$
d. $1.00 \times 10^{-3} \mathrm{~mol} / \mathrm{L}$ of $\mathrm{Ba}(\mathrm{OH})_{2(a q)}$

$$
\mathrm{Ba}(\mathrm{OH})_{2(a q)} \rightarrow \mathrm{Ba}^{2+}{ }_{(a q)}+2 \mathrm{OH}_{(a q)}^{-}
$$

(Ionic Strong Base:
$\left.\left[\mathrm{OH}^{-}\right]=2\left[\mathrm{Ba}(\mathrm{OH})_{2}\right]=2.00 \times 10^{-3} \mathrm{M}\right)$


$$
\begin{array}{ll}
\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right] & \mathrm{pH}=14-\mathrm{pOH} \\
\mathrm{pOH}=-\log \left(2.00 \times 10^{-3}\right) & \mathrm{pH}=14-(2.70)
\end{array}
$$

$$
\mathrm{pOH}=2.70
$$

$$
\mathrm{pH}=11.30
$$

Example 2: Calculate the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$and the $\left[\mathrm{OH}^{-}\right]$for the following solutions.
a. $\mathrm{pH}=4.00$
$\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10^{-\mathrm{pH}}=10^{-4.00}$
$\left.\mathrm{H}_{3} \mathrm{O}^{+}\right]=1.00 \times 10^{-4} \mathrm{M}$
$\mathrm{pOH}=14-\mathrm{pH}$
$\mathrm{pOH}=14-4.00=10.00$
$\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right]$
$\left[\mathrm{OH}^{-}\right]=10^{-\mathrm{pOH}}=10^{-10.00}$
$\left.\mathrm{OH}^{-}\right]=1.00 \times 10^{-10} \mathrm{M}$
b. $\mathrm{pOH}=3.00$
$\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right]$
$\left[\mathrm{OH}^{-}\right]=10^{-\mathrm{pOH}}=10^{-3.00}$

c. $\mathrm{pH}=12.83$
$\mathrm{pH}=14-\mathrm{pOH}$
$\mathrm{pH}=14-3=11.00$
$\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10^{-\mathrm{pH}}=10^{-11.00}$


$$
\begin{gathered}
\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \\
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10^{-\mathrm{pH}}=10^{-12.83}} \\
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1.48 \times 10^{-13} \mathbf{M}} \\
K_{w}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right] \\
{\left[\mathrm{OH}^{-}\right]=\frac{K_{\mathrm{w}}}{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}=\frac{1.0 \times 10^{-14}}{1.48 \times 10^{-13}}} \\
{\left[\mathbf{O H}^{-}\right]=\mathbf{0 . 0 6 7 6 ~ \mathbf { ~ M }}}
\end{gathered}
$$

d. $\mathrm{pOH}=9.67$

$$
\begin{aligned}
\mathrm{pOH} & =-\log [\mathrm{OH}] \\
{\left[\mathrm{OH}^{-}\right] } & =10^{-\mathrm{pOH}}=10^{-9.67}
\end{aligned}
$$

$$
\left.\mathrm{OH}^{-}\right]=2.14 \times 10^{-10} \mathrm{M}
$$

$$
K_{w}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]
$$

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{K_{w}}{\left[\mathrm{OH}^{-}\right]}=\frac{1.0 \times 10^{-14}}{2.14 \times 10^{-10}} \quad\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=4.68 \times 10^{-5} \mathrm{~mol} / \mathrm{L}
$$

## Assignment

$16.2 \& 16.3$ pg. $568-569$ \#9 to 24

## 16.4: Strength of Acids and Bases

Strong Acids: - acids that dissociate completely ( $100 \%$ ) in water.

- when the acid dissociation constant $\left(K_{a}\right)$ is much greater than 1. $\quad\left(K_{a} \gg 1\right)$
- the equilibrium position strongly favours the products.
- at equilibrium, the original acid concentration, $[\mathrm{HA}]_{e q} \approx 0 ;\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]_{e q}=\left[\mathrm{A}^{-}\right]_{e q}=[\mathrm{HA}]_{0}$.
- the conjugate base, $\mathbf{A}^{-}$, of a strong acid, HA is itself a weak base (cannot easily accept protons to do the reverse reaction).
- Note: Strong Acids DO NOT MEAN that they are VERY CORROSIVE. It is the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$that defines acidity.

|  |  | $\begin{aligned} & \text { Strong Acid }\left(K_{a} \gg 1\right) \\ & \left.\qquad K_{a}=\xrightarrow[{\left[\mathbf{H}_{3} \mathbf{O}^{+}\right] \mathbf{A}^{-}}]\right]{[\mathbf{H A}]} 0 \mathbf{M} \end{aligned}$ |  | $+\stackrel{\mathbf{A}_{(a q)}^{-}}{+}{ }_{\text {(Conjugate Base-Weak) }}$ |
| :---: | :---: | :---: | :---: | :---: |
|  | $\underset{(\text { Strong Acid) }}{\mathrm{HA}_{(a q)}}+$ | $\mathrm{H}_{2} \mathrm{O}_{\text {(I) }}$ (Base) | $\rightleftharpoons \underset{(\text { Conjugate Acid) }}{\longrightarrow} \mathrm{H}_{3} \mathrm{O}^{+}{ }_{(a q)}$ |  |
|  | [HA] |  | $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$ | $\left[\mathrm{A}^{-}\right]$ |
| Initial | $X$ |  | 0 | 0 |
| Change | -x |  | + $x$ | + ${ }^{1}$ |
| Equilibrium | 0 |  | $x$ | $\boldsymbol{X}$ |

Examples: Strong Acids: $\mathrm{HClO}_{4(a q)}, \mathrm{HI}_{(a q)}, \mathrm{HBr}_{(a q)}, \mathrm{HCl}_{(a q)}, \mathrm{H}_{2} \mathrm{SO}_{4(a q)}$ and $\mathrm{HNO}_{3(a q)}$
Example 2: Write the dissociation reaction of 0.250 M of $\mathrm{HBr}_{(a q)}$ and determine its $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$.

$$
\mathrm{HBr}_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{(l)} \rightarrow \mathrm{H}_{3} \mathrm{O}_{(a q)}^{+}+\mathrm{Br}_{(a q)}^{-}
$$

(Strong Acid means $[\mathrm{HBr}]_{0}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$)
$[\mathrm{HBr}]_{0}=\mathbf{0 . 2 5 0 ~ M}$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=0.250 \mathrm{M}$
Weak Acids: - acids that dissociate LESS than $\mathbf{1 0 0 \%}$ in water.
-when the acid dissociation constant ( $K_{a}$ ) is less than $1 . \quad\left(K_{a}<1\right)$
-the equilibrium position strongly favours the reactants.
-at equilibrium, the hydronium concentration is much less than the original acid concentration, $[\mathrm{HA}]_{\text {eq }}>\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]_{\text {eq }}$ or $[\mathrm{HA}]_{0} \approx[\mathrm{HA}]_{\text {eq }}$.
-the conjugate base, $\mathbf{A}^{-}$, of a weak acid is itself a stronger weak base (can easily accept protons to do the reverse reaction).
Note: Weak Acids DO NOT MEAN that they are NOT CORROSIVE. It is the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$ that defines acidity. At a high enough concentration, a weak acid can be corrosive.

|  | $\underset{\text { (Weak Acid) }}{\mathrm{HA}_{\text {(aq) }}}+\underset{\text { (Base) }}{\mathrm{H}_{2} \mathrm{O}_{\text {(l) }}}$ | $\rightleftharpoons \quad \underset{(\text { Conjugate Acid) }}{ } \mathrm{H}_{3} \mathrm{O}^{+}{ }_{(a q)}$ | $+\frac{\mathbf{A}_{(a q)}^{-}}{\text {(Conjugate Base-Stronger) }}$ |
| :---: | :---: | :---: | :---: |
|  | [HA] | $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$ | $\left[\mathrm{A}^{-}\right]$ |
| Initial Change | $\begin{array}{rr} x & \\ -y & (\text { where } y \ll x) \\ \hline \end{array}$ | $\begin{gathered} 0 \\ +y \\ \hline \end{gathered}$ | $\begin{gathered} 0 \\ +y \\ \hline \end{gathered}$ |
| Equilibrium | $(x-y) \approx x$ | $y$ | $y$ |

Examples: Some Weak Acids: $\mathrm{HOOCCOOH}_{(a q)}, \mathrm{H}_{2} \mathrm{SO}_{3(a q)}, \mathrm{HSO}_{4}{ }^{-}(a q), \mathrm{H}_{3} \mathrm{PO}_{4(a q)}, \mathrm{HNO}_{2(a q)}, \mathrm{H}_{3} \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}_{7 \text { (aq) }}$, $\mathrm{HF}_{(a q)}, \mathrm{HCOOH}_{(a q)}, \mathrm{C}_{6} \mathrm{H}_{8} \mathrm{O}_{6(a q)}, \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH}_{(a q)}, \mathrm{CH}_{3} \mathrm{COOH}_{(a q)}, \mathrm{H}_{2} \mathrm{CO}_{3(a q)}$, $\mathrm{H}_{2} \mathrm{~S}_{(a q)}, \mathrm{HOCl}_{(a q)}, \mathrm{HCN}_{(a q)}, \mathrm{NH}_{4}^{+}(a q)$, and $\mathrm{H}_{3} \mathrm{BO}_{3(a q)}$
$K_{a}$ and Relative Strength of Some Common Acids and Bases at $25^{\circ} \mathrm{C}$

|  | Acid Name | Acid Formula | Conjugate Base Formula | $K_{a}$ |
| :---: | :---: | :---: | :---: | :---: |
|  | perchloric acid | $\mathrm{HClO}_{4(\text { aq) }}$ | $\mathrm{ClO}_{4}^{-}(a q)$ | Very Large |
|  | hydroiodic acid | $\mathrm{HI}_{(a q)}$ | $\mathrm{I}^{-}(a q)$ | Very Large |
|  | hydrobromic acid | $\mathrm{HBr}_{(\text {aq) }}$ | $\mathrm{Br}^{-}(a q)$ | Very Large |
|  | hydrochloric acid | $\mathrm{HCl}_{(\text {aq) }}$ | $\mathrm{Cl}^{-}(a q)$ | Very Large |
|  | sulfuric acid | $\mathrm{H}_{2} \mathrm{SO}_{4(\text { aq) }}$ | $\mathrm{HSO}_{4}^{-}(a q)$ | Very Large |
| $\qquad$ | nitric acid | $\mathrm{HNO}_{3(a q)}$ | $\mathrm{NO}_{3}^{-}(\mathrm{aq})$ | Very Large |
|  | hydronium ion | $\mathrm{H}_{3} \mathrm{O}^{+}($aq) | $\mathrm{H}_{2} \mathrm{O}_{(l)}$ | , |
|  | oxalic acid | $\mathrm{HOOCCOOH}_{(a q)}$ | $\mathrm{HOOCCOO}^{-}{ }_{(q)}$ | $6.5 \times 10^{-2}$ |
|  | sulfurous acid | $\mathrm{H}_{2} \mathrm{SO}_{3(\text { (aq) }}$ | $\mathrm{HSO}_{3}{ }^{-}$ | $1.5 \times 10^{-2}$ |
|  | hydrogen sulfate ion | $\mathrm{HSO}_{4}^{-}(a q)$ | $\mathrm{SO}_{4}{ }^{2-}$ | $1.2 \times 10^{-2}$ |
|  | chlorous acid | $\mathrm{HClO}_{2(a q)}$ | $\mathrm{ClO}_{2}^{-}{ }_{(a q)}$ | $1.2 \times 10^{-2}$ |
|  | phosphoric acid | $\mathrm{H}_{3} \mathrm{PO}_{4(a q)}$ | $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}{ }_{(a q)}$ | $7.5 \times 10^{-3}$ |
|  | arsenic acid | $\mathrm{H}_{3} \mathrm{AsO}_{4(a q)}$ | $\mathrm{H}_{2} \mathrm{AsO}_{4}^{-}(a q)$ | $5 \times 10^{-3}$ |
|  | monochloracetic acid | $\mathrm{HC}_{2} \mathrm{H}_{2} \mathrm{ClO}_{2}$ | $\mathrm{C}_{2} \mathrm{H}_{2} \mathrm{ClO}_{2}{ }^{-}\left({ }_{\text {aq }}\right.$ | $1.35 \times 10^{-3}$ |
|  | citric acid | $\mathrm{H}_{3} \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}_{7(\text { aq) }}$ | $\mathrm{H}_{2} \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}_{7}^{-}\left({ }_{(a q)}\right.$ | $8.4 \times 10^{-4}$ |
|  | hydrofluoric acid | $\mathrm{HF}_{(a q)}$ | $\mathrm{F}^{-}{ }_{(a q)}$ | $7.2 \times 10^{-4}$ |
|  | nitrous acid | $\mathrm{HNO}_{2(a q)}$ | $\mathrm{NO}_{2}{ }^{-}\left({ }^{\text {aq }}\right.$ | $4.0 \times 10^{-4}$ |
|  | methanoic (formic) acid | $\mathrm{HCOOH}_{(a q)}$ | $\mathrm{HCOO}^{-}(a q)$ | $1.8 \times 10^{-4}$ |
|  | lactic acid | $\mathrm{HC}_{3} \mathrm{H}_{5} \mathrm{O}_{3(a q)}$ | $\mathrm{C}_{3} \mathrm{H}_{5} \mathrm{O}_{3}^{-}($aq) | $1.38 \times 10^{-4}$ |
|  | ascorbic acid (vitamin C) | $\mathrm{H}_{2} \mathrm{C}_{6} \mathrm{H}_{6} \mathrm{O}_{6(a q)}$ | $\mathrm{HC}_{6} \mathrm{H}_{6} \mathrm{O}_{6}^{-}$(aq) | $7.9 \times 10^{-5}$ |
|  | benzoic acid | $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH}_{(a q)}$ | $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COO}^{-}(a q)$ | $6.4 \times 10^{-5}$ |
|  | hydrogen oxalate ion | $\mathrm{HOOCCOO}^{-}{ }_{(q)}$ | $\mathrm{OOCCOO}^{2-}(\mathrm{aq})$ | $6.1 \times 10^{-5}$ |
|  | ethanoic (acetic) acid | $\mathrm{CH}_{3} \mathrm{COOH}_{(a q)}$ | $\mathrm{CH}_{3} \mathrm{COO}^{-}($aq) | $1.8 \times 10^{-5}$ |
|  | dihydrogen citrate ion | $\mathrm{H}_{2} \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}_{7}^{-}{ }_{(a q)}$ | $\mathrm{HC}_{6} \mathrm{H}_{5} \mathrm{O}_{7}{ }^{2-}{ }_{(a q)}$ | $1.8 \times 10^{-5}$ |
|  | hydrated aluminum (III) ion | $\left[\mathrm{Al}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$ | $\left[\mathrm{AlOH}\left(\mathrm{H}_{2} \mathrm{O}\right)_{5}\right]^{2+}$ | $1.4 \times 10^{-5}$ |
|  | propanoic acid | $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}_{(a q)}$ | $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COO}^{-}(a q)$ | $1.3 \times 10^{-5}$ |
|  | hydrogen citrate ion | $\mathrm{HC}_{6} \mathrm{H}_{5} \mathrm{O}_{7}{ }^{2-}{ }_{(a q)}$ | $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}_{7}{ }^{3-}{ }_{(a q)}$ | $4.0 \times 10^{-6}$ |
|  | carbonic acid | $\mathrm{H}_{2} \mathrm{CO}_{3(a q)}$ | $\mathrm{HCO}_{3}^{-}(\mathrm{aq})$ | $4.3 \times 10^{-7}$ |
|  | hydrosulfuric acid | $\mathrm{H}_{2} \mathrm{~S}_{(a q)}$ | $\mathrm{HS}^{-}(a q)$ | $1.0 \times 10^{-7}$ |
|  | hydrogen sulfite ion | $\mathrm{HSO}_{3}^{-}(a q)$ | $\mathrm{SO}_{3}{ }^{2-}\left({ }_{(a q)}\right.$ | $1.0 \times 10^{-7}$ |
|  | dihydrogen arsenate ion | $\mathrm{H}_{2} \mathrm{AsO}_{4}^{-}(\mathrm{aq})$ | $\mathrm{HAsO}_{4}{ }^{2-}{ }_{(a q)}$ | $8 \times 10^{-8}$ |
|  | dihydrogen phosphate ion | $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}(a q)$ | $\mathrm{HPO}_{4}{ }^{2-}(a q)$ | $6.2 \times 10^{-8}$ |
|  | hypochlorous acid | $\mathrm{HOCl}_{(a q)}$ | $\mathrm{OCl}^{-}{ }_{(q q)}$ | $3.5 \times 10^{-8}$ |
|  | hypobromous acid | $\mathrm{HOBr}_{(a q)}$ | $\mathrm{OBr}^{-}(a q)$ | $2 \times 10^{-9}$ |
|  | hydrocyanic acid | $\mathrm{HCN}_{(a q)}$ | $\mathrm{CN}^{-}($aq) | $6.2 \times 10^{-10}$ |
|  | hydrogen arsenate ion | $\mathrm{HAsO}_{4}{ }^{2-}($ aq) | $\mathrm{AsO}_{4}{ }^{3-}(a q)$ | $6 \times 10^{-10}$ |
|  | boric acid | $\mathrm{H}_{3} \mathrm{BO}_{3(\text { aq) }}$ | $\mathrm{H}_{2} \mathrm{BO}_{3}{ }^{-}(\mathrm{aq})$ | $5.8 \times 10^{-10}$ |
|  | ammonium ion | $\mathrm{NH}_{4}^{+}($aq) | $\mathrm{NH}_{3}($ aq) | $5.6 \times 10^{-10}$ |
|  | Phenol | $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}_{(a q)}$ | $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}^{-}{ }_{(q)}$ | $1.6 \times 10^{-10}$ |
|  | hydrogen carbonate ion | $\mathrm{HCO}_{3}^{-}($aq) | $\mathrm{CO}_{3}{ }^{2-}\left({ }_{(q)}\right.$ | $5.6 \times 10^{-11}$ |
|  | hypoiodous acid | $\mathrm{HOI}_{(\text {aq) }}$ | $\mathrm{OI}_{(\text {(aq) }}$ | $2 \times 10^{-11}$ |
|  | hydrogen ascorbate ion | $\mathrm{HC}_{6} \mathrm{H}_{6} \mathrm{O}_{6}^{-}(a q)$ | $\mathrm{C}_{6} \mathrm{H}_{6} \mathrm{O}_{6}{ }^{2-}(a q)$ | $1.6 \times 10^{-12}$ |
|  | hydrogen phosphate ion | $\mathrm{HPO}_{4}{ }^{2-}{ }_{\text {(aq) }}$ | $\mathrm{PO}_{4}{ }^{3-}{ }_{(a q)}$ | $4.8 \times 10^{-13}$ |
|  | water ( $55.49 \mathrm{~mol} / \mathrm{L}$ ) | $\mathrm{H}_{2} \mathrm{O}_{(l)}$ | $\mathrm{OH}^{-}($aq) | $1.0 \times 10^{-14}=K_{w}$ |
|  | hydrogen sulfide ion | $\mathrm{HS}^{-}($aq) | $\mathrm{S}^{2-}($ aq) | $\sim 10^{-19}$ |


| HA |  |  | HA | HA |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{HA}^{+}$ |  | $\mathrm{A}^{-}$ | HA |  |
| HA | $\mathrm{H}^{+}$ | HA |  |  |
| HA |  | HA |  |  |
| HA | HA | HA |  |  |

Concentrated weak acid - a lot present, but little dissociation of acid

| $\mathrm{H}^{+}$ | $\mathrm{A}^{-}$ | $\mathrm{H}^{+}$ | $\mathrm{A}^{-}$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{A}^{-}$ | $\mathrm{H}^{+}$ | $\mathrm{A}^{-}$ | $\mathrm{H}^{+}$ |
| $\mathrm{H}^{+}$ | $\mathrm{A}^{-}$ | $\mathrm{H}^{+}$ | $\mathrm{A}^{-}$ |
| $\mathrm{A}^{-}$ | $\mathrm{H}^{+}$ |  | $\mathrm{H}^{+}$ |
|  |  | $\mathrm{A}^{-}$ | $\mathrm{A}^{-}$ |

Concentrated strong acid-a lot present with a lot of dissociation to form many hydrogen ions

| HA |  |
| :---: | :---: |
| $\mathrm{A}^{-}$ | HA |
| HA |  |
|  | $\mathrm{H}^{+}$ |

Dilute weak acid little acid present with little dissciation of acid


Dilute strong acid much acid present with a high degree of dissociation

Check out Strong and Weak Acids Animations at (http://www.sgc.peachnet.edu/users/larnold/WWW/courses/1212/rev1212.html)

## Relative Strength of Acids and Conjugate Bases:

1. The stronger the acid (the bigger the value of $K_{a}$ ), the weaker its conjugate base.
2. The weaker the acid (the smaller the value of $K_{a}$ ), the stronger its conjugate base.

Example 2: Order the following acids from the strongest to the weakest.

$$
\mathrm{HNO}_{2(a q)}, \mathrm{H}_{2} \mathrm{SO}_{3(a q)}, \mathrm{HClO}_{4(a q)}, \mathrm{HF}_{(a q)}
$$

According to the Acid and Bases Relative Strength Table on the previous page:

$$
\begin{gathered}
\mathrm{HClO}_{4(a q)} \gg \mathrm{H}_{2} \mathrm{SO}_{3(a q)}>\quad \mathrm{HF}_{(a q)}>\mathrm{HNO}_{2(a q)} \\
\left(K_{a}: \text { very large } \gg 1.5 \times \mathbf{1 0}^{-2}>7.2 \times \mathbf{1 0}^{-4}>4.0 \times \mathbf{1 0}^{-4}\right)
\end{gathered}
$$

Example 3: Order the following conjugate base from the strongest to the weakest.

$$
\mathrm{CN}^{-}{ }_{(a q)}, \mathrm{SO}_{4}^{2-}{ }_{(a q)}, \mathrm{Cl}^{-}{ }_{(a q)}, \mathrm{CH}_{3} \mathrm{COO}_{(a q)}^{-}
$$

According to the Acids and Bases Relative Strength Table on the previous page:

$$
\begin{aligned}
& \mathrm{CN}_{(a q)}^{-}>\mathrm{CH}_{3} \mathrm{COO}_{(a q)}^{-}>\mathrm{SO}_{4}{ }^{2-}{ }_{(a q)} \gg \mathrm{Cl}_{(a q)}^{-} \\
&\left(K_{a}: 6.2 \times 10^{-10}<1.8 \times 10^{-5}<1.2 \times 10^{-2} \ll \text { Very Large }\right)<\mathrm{HCN}_{(a q)}<\mathrm{CH}_{3} \mathrm{COOH}_{(a q)}<\mathrm{HSO}_{4(a q)} \ll \mathrm{HCl}_{(a q)}
\end{aligned}
$$

Monoprotic Acids: - acids that can donate a maximum of one proton.
Example 3: Write the dissociation reaction for the following monoprotic acids.
a. $\mathrm{HI}_{(a q)}$
$\mathrm{HI}_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{(I)} \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}{ }_{(a q)}+\mathrm{I}_{(a q)}^{-}$
Direct Arrow because $\mathrm{HI}_{(a q)}$ is a Strong Acid ( $K_{a}$ is very large)
b. $\mathrm{HCOOH}_{(a q)}$
$\mathrm{HCOOH}_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{I})} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}{ }_{(a q)}+\mathrm{HCOO}_{(a q)}^{-}$
Double Arrow because $\mathrm{HCOOH}_{(a q)}$ is a Weak Acid $\left(K_{a}=1.8 \times 10^{-4} \ll 1\right)$

Diprotic Acids: - acids that can donate a maximum of two protons in stepwise dissociation.

(Coniugate Base of Oriqinal Diprotic Acid)

Example 4: Write the stepwise dissociation reaction for the following diprotic acids.
a. $\quad \mathrm{H}_{2} \mathrm{SO}_{4(a q)}$
b. $\mathrm{HOOCCOOH}_{(a q)}$
$\mathrm{H}_{2} \mathrm{SO}_{4(a q)}+\mathrm{H}_{2} \mathrm{O}_{(l)} \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}{ }_{(a q)}+\mathrm{HSO}_{4}^{-}{ }_{(a q)}$
Direct Arrow because $\mathrm{H}_{2} \mathrm{SO}_{4(a q)}$ is a
Strong Acid ( $K_{a 1}$ is very large)
$\mathrm{HSO}_{4}^{-}{ }_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{(I)} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}{ }_{(a q)}+\mathrm{SO}_{4}{ }^{2-}{ }_{(a q)}$
Double Arrow because $\mathrm{HSO}_{4}{ }_{(a q)}$ is a
Weak Acid ( $K_{n 2}=1.2 \times 10^{-2} \ll 1$ )

$$
\begin{aligned}
\mathrm{HOOCCOOH}_{(a q)} & +\mathrm{H}_{2} \mathrm{O}_{(I)}
\end{aligned} \mathrm{H}_{3} \mathrm{O}_{(a q)}+\mathrm{HOOCCOO}_{(a q)}^{-}{ }_{(a q)} \mathrm{HOOCCOO}_{(a q)}^{-}+\mathrm{H}_{2} \mathrm{O}_{(I)} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}_{(a q)}^{+}+\mathrm{OOCCOO}_{(a q)}^{2-}{ }^{(a)}
$$

Double Arrow because both $\mathrm{HOOCCOOH}(a q)$ and $\mathrm{HOOCCOO}^{-}$are Weak Acids ( $K_{a 1}$ and $K_{a 2} \ll 1$ )

Amphoteric Substances: - chemical species that can be an acid or a base.

- all intermediate species of a diprotic acid is an amphoteric substance.

Examples: Some Amphoteric Substances: $\mathrm{HOOCCOO}_{(a q)}^{-}, \mathrm{HSO}_{4}^{-}(a q), \mathrm{HSO}_{3}^{-}{ }_{(a q)}, \mathrm{HCO}_{3}^{-}{ }_{(a q)}, \mathrm{HS}^{-}{ }_{(a q)}$, $\mathrm{HC}_{6} \mathrm{H}_{6} \mathrm{O}_{6}^{-}{ }_{(a q)}$, and $\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}$

## Calculating the pH of Strong Acid Solutions

Major Species: - the predominant species of an acid or a base after dissociation.

- in acid and base dissociation, because they are aqueous, water $\left(\mathrm{H}_{2} \mathbf{O}_{(I)}\right)$ is always listed as a major species.

Maior Species of a Strong Acid: - as strong acid dissociates completely ( $K_{a}>1$ ) in water, the major species of all strong acids are $\mathrm{H}_{3} \mathrm{O}^{+}$and their conjugate bases.

$$
\underset{\text { (Strong Acid) }}{\mathrm{HA}_{(a q)}}+\underset{(\text { Base })}{\mathbf{H}_{2} \mathrm{O}_{(I)}} \longrightarrow \underset{\text { (Conjugate Acid) }}{\mathrm{H}_{3} \mathrm{O}^{+}} \xrightarrow{(\text { Conjugate Base-Weak) }}
$$

Example 5: List the major species $\mathrm{H}_{2} \mathrm{SO}_{4(a q)}$, and calculate its pH if it has a concentration of $1.00 \times 10^{-5} \mathrm{M}$.

$$
\mathrm{H}_{2} \mathrm{SO}_{4(a q)}+\mathrm{H}_{2} \mathrm{O}_{(l)} \rightarrow \mathrm{H}_{3} \mathrm{O}_{(a q)}^{+}+\mathbf{H S O}_{4}^{-}(a q)
$$

Since $\underline{H}_{2} \underline{S O}_{4}$ is a strong acid, the major species are: $\mathrm{H}_{3} \mathrm{O}_{(a q)}^{+}, \mathrm{HSO}_{4}^{-}{ }_{(a q)}$ and $\mathrm{H}_{2} \mathrm{O}_{\text {(ll }}$.
(Even if $\mathrm{H}_{2} \mathrm{SO}_{4}$ is a diprotic acid, it dissociates one proton at a time. The conjugate base, $\mathrm{HSO}_{4}^{-}$, is a weak acid. Weak acids dissociate differently than strong acids - next section.)

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left[\mathrm{H}_{2} \mathrm{SO}_{4}\right]_{0}=1.00 \times 10^{-5} \mathrm{M}
$$

$$
\begin{aligned}
& \mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \\
& \mathrm{pH}=-\log \left(1.00 \times 10^{-5}\right)
\end{aligned}
$$

$$
\mathrm{pH}=5.00
$$

Example 6: Determine the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$and/or $\left[\mathrm{OH}^{-}\right]$concentrations of the following solutions at $25^{\circ} \mathrm{C}$.
a. $[\mathrm{HCl}]=0.350 \mathrm{~mol} / \mathrm{L}$

$$
\mathrm{HCl}_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{(l)} \rightarrow \mathrm{H}_{3} \mathrm{O}_{(a q)}+\mathrm{Cl}_{(a q)}^{-}
$$

$\left(\right.$ Strong Acid: $\left.[\mathrm{HCl}]_{0}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=0.350 \mathrm{M}\right)$

$$
\begin{aligned}
K_{w} & =\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right] \\
{\left[\mathrm{OH}^{-}\right] } & =\frac{K_{w}}{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}=\frac{1.0 \times 10^{-14}}{0.350}
\end{aligned}
$$

$$
\left[\mathrm{OH}^{-}\right]=2.86 \times 10^{-14} \mathrm{~mol} / \mathrm{L}
$$

b. $[\mathrm{NaOH}]=0.0750 \mathrm{M}$

$$
\mathrm{NaOH}_{(a q)} \rightarrow \mathrm{Na}_{(a q)}^{+}+\mathrm{OH}_{(a q)}^{-}
$$

(Ionic Strong Base: $[\mathrm{NaOH}]_{0}=\left[\mathrm{OH}^{-}\right]=0.0750 \mathrm{M}$ )

$$
\begin{aligned}
K_{w}= & {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right] } \\
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] } & =\frac{K_{w}}{\left[\mathrm{OH}^{-}\right]}=\frac{1.0 \times 10^{-14}}{0.0750} \\
& \frac{\left.\mathrm{H}_{3} \mathrm{O}^{+}\right]=1.33 \times 10^{-13} \mathrm{~mol} / \mathrm{L}}{}
\end{aligned}
$$

Oxoacids: - acids where the donating proton is attached to an oxygen atom.

- most acids are oxoacids because of the strong electronegativity of the oxygen atom, the hydrogen atom is more readily to leave as $\mathrm{H}^{+}$ion.
Example: Sulfuric Acid $\left(\mathrm{H}_{2} \mathrm{SO}_{4}(a q)\right.$ ), successively donate protons to finally reach $\mathrm{SO}_{4}{ }^{2-}(a q)$


Organic Acids: - acids of organic compounds, commonly known as carboxylic acids.

- alcohols can also be considered as organic acids, but they are really weak. This is because carboxylic acids have double-bonded oxygen for resonance to occur, whereas alcohols only contain single-bonded oxygen.

Example: Ethanoic (Acetic) Acid is compared to Phenol



## Assignment

16.4 pg. 569 \#25 to 36; pg. 571 \#86

## 16.5: Weak Acids and Acid Ionization Constants

Major Species of a Weak Acid: - since weak acid do not dissociate completely $\left(K_{a}<1\right)$ in water, the major species of all weak acids are their original form and water.

## Procedure to calculate pH of Weak Acid Solutions:

1. List all the major species from all weak acids, including water.
2. Determine which species has the highest $K_{a}$. This is the Strongest Acid (SA) of the list.
3. Write the Brønsted-Lowry dissociation of this Strongest Acid.
4. Set up the ICE Box and the equilibrium expression.
5. If the original weak acid concentration, $[H A]_{0}$, is much larger than $K_{\underline{a}}$, we can approximate by assuming $[H A]_{e q}=\left([H A]_{\underline{0}}-x\right) \approx[H A]_{0}$. Thereby, simplifying the calculation. (A general rule of thumb: if $[H A]_{0} \geq \mathbf{1 0 0 0} \times K_{a}$, we can use the approximation.)
6. Find the concentration of $\mathrm{H}_{3} \mathrm{O}^{+}$.
7. Verify any approximation made by using the $5 \%$ rule. $\quad\left(\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]^{5}}{[\mathbf{H A}]_{0}} \times \mathbf{1 0 0 \%} \leq \mathbf{5 \%}\right)$

Example 1: Determine the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$, and pH of $0.200 \mathrm{~mol} / \mathrm{L}$ of $\mathrm{HF}_{(a q)}\left(K_{a}=7.2 \times 10^{-4}\right)$.
Major Species: $\mathrm{HF}_{(a q)}, \mathrm{H}_{2} \mathrm{O}_{(I)}$
Strongest Acid: $\mathrm{HF}\left(K_{a}=7.2 \times 10^{-4}\right) \quad\left(K_{a}\right.$ for $\mathrm{H}_{2} \mathrm{O}$ is $\left.1.0 \times 10^{-14}\right)$
HF is a weak acid and undergoes Brønsted-Lowry Dissociation.

|  | $\mathrm{HF}_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{(l)} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}{ }_{(a q)}+\mathrm{F}^{-}{ }_{(a q)}$ |  |  |
| :---: | :---: | :---: | :---: |
|  | [HF] | $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$ | [ $\mathrm{F}^{-}$] |
| Initial Change | $\begin{gathered} 0.200 \mathrm{M} \\ -x \end{gathered}$ | $\begin{gathered} 0 \\ +x \end{gathered}$ | $\begin{gathered} 0 \\ +x \end{gathered}$ |
| Equilibrium | (0.2-x) | $x$ | $x$ |

CANNOT use Approximation:
$\frac{[\mathrm{HF}]_{0}}{K_{a}}=\frac{0.200 \mathrm{M}}{7.2 \times 10^{-4}}=\mathbf{2 7 7 . 8}<\mathbf{1 0 0 0}$
Have to use $(0.2-x)$ in the


$$
\begin{aligned}
\left(1.44 \times 10^{-4}\right)-\left(7.2 \times 10^{-4}\right) x & =x^{2} \\
x^{2}+\left(7.2 \times 10^{-4}\right) x-\left(1.44 \times 10^{-4}\right) & =0
\end{aligned}
$$

(Quadratic Equation: Apply the Quadratic Formula!)

$$
\begin{aligned}
& x=\frac{-b \pm \sqrt{b^{2}-4 a c}}{2 a} \quad a=1 \quad b=7.2 \times 10^{-4} \quad c=-1.44 \times 10^{-4} \\
& x=\frac{-\left(7.2 \times 10^{-4}\right) \pm \sqrt{\left(7.2 \times 10^{-4}\right)^{2}-4(1)\left(-1.44 \times 10^{-4}\right)}}{2(1)} \\
& x=\mathbf{0 . 0 1 1 6 4 5 3 9 8 8} \quad x=-0.0247307976 \text { (omit negative } x)
\end{aligned}
$$

$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\mathbf{0 . 0 1 1 6 ~ \mathrm { mol } / \mathrm { L }}$
$\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$
$\mathrm{pH}=-\log (0.0116)$
$\mathrm{pH}=\mathbf{1 . 9 3}$

Verify that we could NOT use Approximation:

$$
\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{[\mathrm{HF}]_{0}} \times 100 \%=\frac{0.0116 \mathrm{M}}{0.200 \mathrm{M}} \times 100 \%=5.8 \%>5 \%
$$

Therefore, approximation would NOT be appropriate.

Percent Dissociation: - the amount of $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$dissociated from the original $[\mathrm{HA}]_{0}$ expressed in percentage.

- strong acids will have $\%$ dissociation $=100 \%$.
- weak acids will have $\%$ Dissociation $<100 \%$

> Percent Dissociation of Acids $\%$ Dissociation $=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{[\mathrm{HA}]_{0}} \times 100 \%$

Example 2: Determine the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$and pH of an acid mixture of $0.500 \mathrm{~mol} / \mathrm{L} \mathrm{HOBr}_{(a q)}\left(K_{a}=2 \times 10^{-9}\right)$ of $0.200 \mathrm{~mol} / \mathrm{L}^{\text {of }} \mathrm{CH}_{3} \mathrm{COOH}_{(a q)}\left(K_{a}=1.8 \times 10^{-5}\right)$. Calculate the $\%$ dissociation of this acid mixture.
Major Species: $\mathrm{HOBr}_{(a q)}, \mathrm{CH}_{3} \mathrm{COOH}_{(a q)}, \mathrm{H}_{2} \mathrm{O}_{(l)}$
Strongest Acid: $\mathrm{CH}_{3} \mathrm{COOH}\left(K_{a}=\mathbf{1 . 8} \times \mathbf{1 0}^{-5}\right) \quad\left(K_{a}\right.$ for HOBr and $\mathrm{H}_{2} \mathrm{O}$ are $2 \times 10^{-9}$ and $\left.1.0 \times 10^{-14}\right)$
$\mathrm{CH}_{3} \mathrm{COOH}$ is a weak acid and undergoes Brønsted-Lowry Dissociation. CAN use Approximation:

$$
\mathrm{CH}_{3} \mathrm{COOH}_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{(l)} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}_{(a q)}^{+}+\mathrm{CH}_{3} \mathrm{COO}_{(a q)}^{-}
$$

|  | $\left[\mathrm{CH}_{3} \mathrm{COOH}\right]$ | $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$ | $\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]$ |
| :--- | :---: | :---: | :---: | :---: |
| Initial | 0.200 M | 0 | 0 <br> $+x$ |
| Change | $-x$ | $+x$ | $+\boldsymbol{x}$ |
| Equilibrium | $(0.2-x)$ | $x$ | $\boldsymbol{x}$ |

$K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]} \quad 1.8 \times 10^{-5}=\frac{(x)(x)}{(0.2-x)} \approx \frac{x^{2}}{(0.2)}$

$$
\begin{aligned}
\frac{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]_{0}}{K_{a}} & =\frac{0.200 \mathrm{M}}{1.8 \times 10^{-5}} \\
& =\mathbf{1 1 1 1 1 \geq \mathbf { 1 0 0 0 }}
\end{aligned}
$$

Use 0.2 in the denominator, because $(0.2-x) \approx 0.2$ [ $x$ is so small compared to 0.2 M ]
$1.8 \times 10^{-5}(0.2) \approx x^{2}$
$3.6 \times 10^{-6} \approx x^{2}$
$x \approx \sqrt{3.6 \times 10^{-6}}$
$\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$
$\mathrm{pH}=-\log (0.00190)$
Verify that we could use Approximation:
$\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]_{0}} \times 100 \%=\frac{0.00190 \mathrm{M}}{0.200 \mathrm{M}} \times 100 \%$
$=0.95 \% \leq 5 \%$
Therefore, approximation would be appropriate.
$\boldsymbol{x} \approx \mathbf{0 . 0 0 1 9 0}$
$\%$ Dissociation $=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right\rfloor}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]_{0}} \times 100 \%$
$\%$ Dissociation $=\frac{0.00190 \mathrm{M}}{0.200 \mathrm{M}} \times 100 \%$
$\%$ Dissociation $=0.95 \%$

Example 3: A $0.0500 \mathrm{~mol} / \mathrm{L}$ of an unknown acid, HA, has a percent dissociation of $0.38 \%$. What is the acid dissociation constant of this acid?
Major Species: $\mathrm{HA}_{(a q)}, \mathbf{H}_{\mathbf{2}} \mathrm{O}_{(I)}$
Strongest Acid: HA ( $K_{a}=$ ? )
( $K_{a}$ for $\mathrm{H}_{2} \mathrm{O}$ is $1.0 \times 10^{-14}$ and has a $0.00001 \%$ dissociation)
HA is a weak acid and undergoes Bronsted-Lowry Dissociation.

|  | $\mathrm{A}_{(a q)}+\mathrm{H}_{2} \mathrm{O}$ | $\mathrm{H}_{3} \mathrm{O}^{+}{ }_{(a q)}+$ | $+\mathbf{A}^{-}(a q)$ |
| :---: | :---: | :---: | :---: |
|  | [HA] | $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$ | [ $\mathbf{A}^{-}$] |
| Initial | 0.0500 M | 0 | - |
| Change | $-1.9 \times 10^{-4}$ | $+1.9 \times 10^{-4}$ | $1.9 \times 10^{-4}$ |
| Equilibrium | 0.04981 M | $1.9 \times 10^{-4} \mathrm{M}$ | $1.9 \times 10^{-4} \mathrm{M}$ |

$\%$ Dissociation $=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{[\mathrm{HA}]_{0}} \times 100 \%$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=(\%$ Dissociation $)[\mathrm{HA}]_{0} / 100 \%$ $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=(0.38 \%)(0.0500 \mathrm{M}) / 100 \%$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1.9 \times 10^{-4} \mathrm{M}=\left[\mathrm{A}^{-}\right]$
$K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}=\frac{\left(1.9 \times 10^{-4}\right)\left(1.9 \times 10^{-4}\right)}{(0.04981)}$ $K_{a}=7.2 \times 10^{-}$

Polyprotic Acids: - acids that can donate more than one protons.

- this includes all diprotic and triprotic acids (acids that can donate three protons).
- polyprotic acids dissociate one proton at a time. Each successive proton donation has its own $K_{a}$, which gets smaller until the last proton is donated. ( $K_{a 1}>K_{a 2}>K_{a 3}>\ldots$ ).
- the intermediates (conjugate bases of each dissociation except the last one) are themselves acids. Thus, diprotic acid can generate one amphoteric species, and triprotic acid can generate two amphoteric species.
- except for sulfuric acid (because $K_{a 1}$ is very large and $K_{a 2}$ is small), all polyprotic acids ${ }^{\prime}\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$are calculated from their $K_{\underline{a 1}}$ because successive proton donation from smaller subsequent $K_{a}$ do not amount to any significant increase in the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$.

Examples: Some Polyprotic Acids:
a. Diprotic Acids: $\mathrm{H}_{2} \mathrm{SO}_{4(a q)}, \mathrm{HOOCCOOH}_{(a q)}, \mathrm{H}_{2} \mathrm{SO}_{3(a q)}, \mathrm{H}_{2} \mathrm{C}_{6} \mathrm{H}_{6} \mathrm{O}_{6(a q)}, \mathrm{H}_{2} \mathrm{CO}_{3(a q)}, \mathrm{H}_{2} \mathrm{~S}_{(a q)}$

Diprotic Amphoteric Intermediates: $\mathrm{HSO}_{4}^{-}{ }_{(a q)}, \mathrm{HOOCCOO}^{-}{ }_{(a q)}, \mathrm{HSO}_{3}^{-}{ }_{(a q)}, \mathrm{HC}_{6} \mathrm{H}_{6} \mathrm{O}_{6}^{-}{ }_{(a q)}$,

$$
\mathrm{HCO}_{3}^{-}{ }_{(a q)}, \mathrm{HS}_{(a q)}^{-}
$$

b. Triprotic Acids: $\mathrm{H}_{3} \mathrm{PO}_{4(a q)}, \mathrm{H}_{3} \mathrm{AsO}_{4(a q)}, \mathrm{H}_{3} \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}_{7(a q)}, \mathrm{H}_{3} \mathrm{BO}_{3(a q)}$

Triprotic Amphoteric Intermediates: $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}{ }_{(a q)}, \mathrm{HPO}_{4}{ }^{2-}{ }_{(a q)}, \mathrm{H}_{2} \mathrm{AsO}_{4}{ }^{-}{ }_{(a q)}, \mathrm{HAsO}_{4}{ }^{2-}{ }_{(a q)}$,

$$
\mathrm{H}_{2} \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}_{7}^{-}(a q), \mathrm{HC}_{6} \mathrm{H}_{5} \mathrm{O}_{7}^{2-}{ }_{(a q)}, \mathrm{H}_{2} \mathrm{BO}_{3}^{--}(a q), \mathrm{HBO}_{3}^{2-}{ }_{(a q)}
$$

Example 1: Determine the pH of 0.0500 M of sulfuric acid $\left(\mathrm{H}_{2} \mathrm{SO}_{4}(a q)\right)$ and the concentrations of $\mathrm{HSO}_{4}^{-}{ }_{(a q)}$, and $\mathrm{SO}_{4}{ }^{2-}(a q)$. The acid dissociation constant is $K_{a 2}=1.2 \times 10^{-2}$.

$$
\mathrm{H}_{2} \mathrm{SO}_{4(a q)}+\mathrm{H}_{2} \mathrm{O}_{(l)} \rightarrow \mathrm{H}_{3} \mathrm{O}_{(a q)}^{+}+\mathbf{H S O}_{4}^{-}(a q)
$$

Since $\underline{H}_{2} \underline{S O}_{4}$ is a strong acid, the major species are: $\mathrm{H}_{3} \mathrm{O}^{+}{ }_{(a q)}, \mathbf{H S O}_{4}{ }^{-}(a q)$ and $\mathrm{H}_{2} \mathrm{O}_{(1)}$.

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left[\mathrm{H}_{2} \mathrm{SO}_{4}\right]_{0}=0.0500 \mathrm{M}
$$

$$
\begin{aligned}
& \mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \\
& \mathrm{pH}=-\log (0.0500)
\end{aligned}
$$

$$
\mathrm{pH}=1.30\left(\text { after } K_{a 1}\right)
$$

Next, we have to calculate $\left[\mathrm{HSO}_{4}{ }^{-}\right],\left[\mathrm{SO}_{4}{ }^{2-}\right]$ and the final pH after the last proton donation.
Major Species: $\mathrm{HSO}_{4}^{-}{ }_{(a q)}, \mathbf{H}_{2} \mathrm{O}_{(I)} \quad$ Strongest Acid: $\mathrm{HSO}_{4}^{-}{ }_{(a q)}\left(K_{a 2}=\mathbf{1 . 2} \times \mathbf{1 0}^{\mathbf{- 2}}\right)$ $\mathrm{HSO}_{4}{ }^{-}$is a weak acid (Brønsted-Lowry Dissociation).

|  | $\mathrm{HSO}_{4}^{-}{ }_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{(l)} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}{ }_{(a q)}+\mathrm{SO}_{4}{ }^{\mathbf{2 -}}{ }_{(a q)}$ |  |  |
| :---: | :---: | :---: | :---: |
|  | $\left[\mathrm{HSO}_{4}{ }^{-}\right]$ | $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$ | [ $\mathrm{SO}_{4}{ }^{2-}$ ] |
| Initial | 0.0500 M | 0.0500 M | 0 |
| Change | -X | + $X$ | + $X$ |
| Equilibrium | (0.05-x) | (0.05 + x ) | $x$ |

CANNOT use Approximation:

$$
\begin{aligned}
\frac{\left[\mathrm{HSO}_{4}\right]_{0}}{K_{a 2}} & =\frac{0.0500 \mathrm{M}}{1.2 \times 10^{-2}} \\
& =4.167<\mathbf{1 0 0 0}
\end{aligned}
$$



Final $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=0.0500 \mathrm{M}\left(\right.$ from $\left.K_{a 1}\right)+0.00851 \mathrm{M}\left(\right.$ from $\left.K_{a 2}\right)$


$$
\begin{array}{r}
{\left[\mathrm{HSO}_{4}{ }^{-}\right]_{e q}=} \\
\\
{\left[\mathrm{HSO}_{4}^{-}\right]_{\text {eq }}=0.0500 \mathrm{M}-0.00851 \mathrm{M}} \\
{\left[\mathrm{SO}_{4}{ }^{2-}\right]_{\text {eq }}=\mathbf{0 . 0 0 5 8 5} \mathrm{M}}
\end{array}
$$

Final $\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=-\log (0.0585)$
Final pH = 1.23
(different from 1.30 of the pH at $K_{a 1}$ )

From the last two examples, we can see that sulfuric acid $\left(\mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{aq})\right.$ ) requires the calculation of $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$in both steps of the dissociation. Other polyprotic acids, such as $\mathrm{H}_{3} \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}_{7}(\mathrm{aq})$ only require the first dissociation step to calculate the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$.

## Assignment

16.5 pg. 569-570 \#37 to 52; pg. 571 \#93

## 16.6 \& 16.7: Weak Bases and Base Ionization Constants \& The Relationship Between the Ionization and their Conjugate Bases

Strong Bases: - bases that dissociate completely ( $\mathbf{1 0 0 \%}$ ) in water.

- all alkali bases (Group IA cations with $\mathbf{O H}^{-}$) and some alkaline bases (Group IIA cations with $\mathbf{O H}^{-}$) are considered as strong bases because they are ionic compound that dissociates completely.

Examples: Strong Ionic Bases:
a. Alkali Bases: $\mathrm{LiOH}_{(a q)}, \mathrm{NaOH}_{(a q)}, \mathrm{KOH}_{(a q)}, \mathrm{RbOH}_{(a q)}$, and $\mathrm{CsOH}_{(a q)}$
(gives off 1 mole of $\mathrm{OH}^{-}$when 1 mole of alkali base is dissolved)

$$
\mathrm{NaOH}_{(a q)} \rightarrow \mathrm{Na}_{(a q)}^{+}+\mathbf{O H}_{(a q)}^{-} \quad \mathrm{KOH}_{(a q)} \rightarrow \mathrm{K}_{(a q)}^{+}+\mathbf{O H}_{(a q)}^{-}
$$

b. Alkaline Bases: $\mathrm{Ca}(\mathrm{OH})_{2(a q)}, \mathrm{Ba}(\mathrm{OH})_{2(a q)}, \mathrm{Sr}(\mathrm{OH})_{2(a q)}$
(gives off 2 moles of $\mathrm{OH}^{-}$when 1 mole of alkaline base is dissolved)

$$
\mathrm{Ba}(\mathbf{O H})_{2(a q)} \rightarrow \mathrm{Ba}^{2+}{ }_{(a q)}+2 \mathbf{O H}_{(a q)}^{-} \quad \mathrm{Sr}(\mathbf{O H})_{2(a q)} \rightarrow \mathrm{Sr}^{2+}{ }_{(a q)}+\mathbf{2} \mathbf{O H}_{(a q)}^{-}
$$

Major Species of a Strong Base: - as alkali- and alkaline bases dissociate completely in water, the major species of all strong bases are $\mathbf{O H}^{-}$and water.

- special care must be taken with alkaline bases as they generate 2 moles of $\mathrm{OH}^{-}$per 1 mole of solid dissolved.
$\underset{\text { (Strong Base) }}{\mathrm{MOH}_{(a q)}} \xrightarrow[\text { (Spectator Metal Cation) }]{\mathrm{M}^{+}}+\underset{\text { (Maq) }}{ }+\underset{\text { (Major Species of Strong Base) }}{\mathbf{O H}^{-}}$

Example 1: List the major species $\mathrm{NaOH}_{(a q)}$, and calculate its $\mathrm{pH}, \mathrm{pOH},\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$and $\left[\mathrm{OH}^{-}\right]$if it has a concentration of $1.00 \times 10^{-4} \mathrm{M}$.

$$
\mathrm{NaOH}_{(a q)} \rightarrow \mathrm{Na}^{+}{ }_{(a q)}+\mathrm{OH}_{(a q)}^{-}
$$

Since NaOH is a strong base, the major species are: $\mathbf{O H}^{-}{ }_{(a q)}$ and


Example 2: List the major species $\mathrm{Sr}(\mathrm{OH})_{2(a q)}$, and calculate its $\mathrm{pH}, \mathrm{pOH},\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$and $\left[\mathrm{OH}^{-}\right]$if it has a concentration of $1.00 \times 10^{-4} \mathrm{M}$.

$$
\mathrm{Sr}(\mathrm{OH})_{2(a q)} \rightarrow \mathrm{Sr}^{2+}{ }_{(a q)}+\mathbf{2} \mathbf{O H}_{(a q)}^{-}
$$



$$
\begin{array}{rl}
{\left[\mathbf{O H}^{-}\right]=\mathbf{2} \times\left[\mathrm{Sr}(\mathrm{OH})_{2}\right]_{0}=\mathbf{2 . 0 0} \times \mathbf{1 0}^{-4} \mathbf{M}} & \mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right] \\
\mathrm{pOH}=-\log \left(2.00 \times 10^{-4}\right) \quad \mathbf{p O H}=\mathbf{3 . 7 0} \\
K_{w} & =\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]
\end{array} l \begin{array}{ll}
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{K_{w}}{\left[\mathrm{OH}^{-}\right]}=\frac{1.0 \times 10^{-14}}{2.00 \times 10^{-4}}} & \mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \\
\mathrm{pH}=-\log \left(5.00 \times 10^{-11}\right) \\
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\mathbf{5 . 0 0} \times 10^{-11} \mathbf{~ m o l} / \mathrm{L}} & \mathrm{pH}=\mathbf{1 0 . 3}
\end{array}
$$

Weak Bases: - bases that dissociate LESS than $100 \%$ in water.

- when the base dissociation constant ( $K_{b}$ ) is less than $1 . \quad\left(K_{b}<1\right)$
- the equilibrium position strongly favours the reactants.
- at equilibrium, the hydroxide concentration is much less than the original base concentration, $[\mathrm{OH}]_{e q}<[\mathrm{B}]_{e q}$ or $[\mathrm{B}]_{0} \approx[\mathrm{~B}]_{e q}$.
- the conjugate acid, $\mathrm{HA}^{-}$, of a weak base is itself a stronger weak acid (can easily donate protons to do the reverse reaction).

$$
\underset{\text { (Weak Base) }}{\mathrm{B}_{(a q)}}+\underset{(\text { Acid })}{\mathbf{H}_{2} \mathrm{O}_{(l)}} \stackrel{\rightleftharpoons}{\text { (Conjugate Base) }} \underset{(\text { Conjugate Acid-Stronger) }}{\mathrm{OH}^{-}}
$$

|  | $[\mathrm{B}]$ | $\left[\mathrm{OH}^{-}\right]$ | $\left[\mathrm{HB}^{+}\right]$ |
| :--- | :---: | :---: | :---: |
| Initial | $x$ | 0 | 0 |
| Change | $-y \quad($ where $y \ll x)$ | $+y$ | $+y$ |
| Equilibrium | $(x-y) \approx x$ | $y$ | $y$ |

Examples: Some Weak Bases: $\mathrm{HOOCCOO}_{(a q)}^{-}, \mathrm{HSO}_{3}^{-}{ }_{(a q)}, \mathrm{HSO}_{4}^{-}{ }_{(a q)}, \mathrm{H}_{2} \mathrm{PO}_{4}^{-}{ }_{(a q)}, \mathrm{NO}_{2}^{-}{ }_{(a q)}, \mathrm{HCO}_{3}^{-}{ }_{(a q)}$, $\mathrm{H}_{2} \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}_{7}^{-}{ }_{(a q)}, \mathrm{F}^{-}{ }_{(a q)}, \mathrm{HCOO}^{-}{ }_{(a q)}, \mathrm{C}_{6} \mathrm{H}_{7} \mathrm{O}_{6}^{-}{ }_{(a q)}, \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COO}^{-}{ }_{(a q)}, \mathrm{CO}_{3}{ }^{2-}{ }_{(a q)}$ $\mathrm{CH}_{3} \mathrm{COO}^{-}{ }_{(a q)}, \mathrm{HS}^{-}{ }_{(a q)}, \mathrm{OCl}^{-}{ }_{(a q)}, \mathrm{CN}^{-}{ }_{(a q)}, \mathrm{NH}_{3}{ }_{(a q)}$, and $\mathrm{NO}_{3}^{-}{ }_{(a q)}$

Base Dissociation Constant ( $K_{b}$ ): - the equilibrium constant of a dissociation of a weak base in water.

- $K_{b}$ of a weak base can be calculated from $K_{a}$ of its conjugate acid and $K_{w}$.

$$
\begin{aligned}
& \mathbf{B}_{(a q)}+\mathbf{H}_{2} \mathbf{O}_{(l)} \rightleftharpoons \mathbf{O H}^{-}(a q) \quad+\mathbf{H B}^{+}{ }_{(a q)} \quad K_{b}=\frac{\left[\mathbf{O H}^{-} \mathbf{T} \mathbf{H B}^{+}\right]}{[\mathbf{B}]} \\
& \text { (Weak Base) (Acid) (Conjugate Base) (Conjugate Acid) } \\
& \mathrm{HB}^{+}{ }_{(a q)}+\mathbf{H}_{2} \mathrm{O}_{(\mathrm{l})} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}{ }_{(a q)} \quad+\quad \mathbf{B}_{(a q)} \quad K_{a}=\frac{\left.\left[\mathbf{H}_{3} \mathbf{O}^{+}\right] \mathbf{B}\right]}{\left[\mathbf{H B}^{+}\right]} \\
& \text {(Weak Acid) (Base) (Conjugate Acid) (Conjugate Base) } \\
& \boldsymbol{K}_{a} \times \boldsymbol{K}_{\boldsymbol{b}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right][\mathrm{B}]}{\left.\mathrm{HB}^{+}\right]} \times \frac{\left.\left[\mathrm{OH}^{-}\right] \mathrm{HB}^{+}\right]}{[\mathrm{B}]}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=\boldsymbol{K}_{w} \\
& K_{w}=K_{a} \times \boldsymbol{K}_{b}
\end{aligned}
$$

Maior Species of a Weak Base: - since weak acid do not dissociate completely $\left(K_{b}<1\right)$ in water, the major species of all weak bases are their original form and water.

## Procedure to calculate pH of Weak Base Solutions:

1. List all the major species from all weak bases, including water.
2. Calculate $K_{b}$ from all weak bases using $K_{w}=K_{a} \times K_{b}$
3. Determine which species has the highest $K_{b}$. This is the Strongest Base (SB) of the list.
4. Write the Brønsted-Lowry dissociation of this Strongest Base
5. Set up the ICE Box and the equilibrium expression.
6. If the original weak base concentration, $[\mathrm{B}]_{0}$, is much larger than $K_{b}$, we can approximate by assuming $\sqrt{B}]_{e q}=\left([B]_{0}-x\right) \approx[B]_{\underline{0}}$. Thereby, simplifying the calculation. (A general rule of thumb: if $[B]_{0} \geq 1000 \times K_{b}$, we can use the approximation.)
7. Find the concentration of $\mathrm{OH}^{-}$.
8. Verify any approximation made by using the $5 \%$ rule. $\quad\left(\frac{\left[\mathrm{OH}^{-}\right]^{5}}{[\mathrm{~B}]_{0}} \times 100 \% \leq 5 \%\right)$

Example 3: Determine the $\left[\mathrm{OH}^{-}\right],\left[\mathrm{H}_{3} \mathrm{O}^{+}\right], \mathrm{pOH}, \mathrm{pH}$ and $\%$ dissociation of $0.200 \mathrm{~mol} / \mathrm{L}$ of $\mathrm{NaCN}(a q)$. $\left(K_{a}\right.$ of $\left.\mathrm{HCN}=6.2 \times 10^{-10}\right)$.

NaCN dissociates completely in water:

$$
\mathrm{NaCN}_{(a q)} \rightarrow \mathrm{Na}_{(a q)}^{+}+\mathbf{C N}_{(a q)}^{-}(\text {Weak Base })
$$

Major Species: $\mathbf{C N}^{-}{ }_{(a q)}, \mathrm{H}_{2} \mathrm{O}_{(I)}$
$K_{b}=\frac{K_{w}}{K_{a}}=\frac{1.00 \times 10^{-14}}{6.2 \times 10^{-10}} \quad K_{b}=1.613 \times 10^{-5}$
(taking a few more decimal places to avoid round off errors)
Strongest Base: $\mathbf{C N}^{-}\left(K_{b}=\mathbf{1 . 6 1 3} \times \mathbf{1 0}^{-5}\right) \quad\left(K_{b}\right.$ for $\mathrm{H}_{2} \mathrm{O}$ is $\left.K_{w}=1.0 \times 10^{-14}\right)$
$\mathrm{CN}^{-}$is a weak base and undergoes Brønsted-Lowry Dissociation.
CAN use Approximation:

$$
\mathbf{C N}^{-}(a q)+\mathbf{H}_{2} \mathrm{O}_{(l)} \rightleftharpoons \mathrm{HCN}_{(a q)}+\mathrm{OH}_{(a q)}^{-}
$$

|  | $\left[\mathrm{CN}^{-}\right]$ |  | $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$ | $\left[\mathrm{OH}^{-}\right]$ |
| :--- | :---: | :---: | :---: | :---: |
| Initial | $\mathbf{0 . 2 0 0} \mathbf{M}$ | 0 |  |  |
| Change | $-\boldsymbol{x}$ |  | 0 <br> $+x$ |  |
| Equilibrium | $(\mathbf{0 . 2}-\boldsymbol{x})$ |  | $x$ | $\boldsymbol{x}$ |

$K_{b}=\frac{[\mathrm{HCN}]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{CN}^{-}\right]} \quad 1.613 \times 10^{-5}=\frac{(x)(x)}{(0.2-x)} \approx \frac{x^{2}}{(0.2)}$

$$
\begin{aligned}
1.613 \times 10^{-5}(0.2) & \approx x^{2} \\
3.226 \times 10^{-6} & \approx x^{2} \\
x & \approx \sqrt{3.226 \times 10^{-6}} \\
\boldsymbol{x} & \approx \mathbf{0 . 0 0 1 8}
\end{aligned}
$$

$$
\begin{aligned}
\frac{\left[\mathrm{CN}^{-}\right]_{0}}{K_{b}} & =\frac{0.200 \mathrm{M}}{1.613 \times 10^{-5}} \\
& =\mathbf{1 2 3 9 9} \geq \mathbf{1 0 0 0}
\end{aligned}
$$

Use 0.2 in the denominator,
because $(0.2-x) \approx 0.2 \quad[x$ is so small compared to 0.2 M ]
$\left[\mathrm{OH}^{-}\right]=0.0018 \mathrm{~mol} / \mathrm{L}=1.8 \mathrm{mmol} / \mathrm{L}$

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

$$
\mathrm{pOH}=-\log (0.0018)
$$

$$
\mathrm{pOH}=2.75
$$

Verify that we could use Approximation:

$$
\begin{array}{r}
\frac{\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{CN}^{-}\right]_{0}} \times 100 \%=\frac{0.0018 \mathrm{M}}{0.200 \mathrm{M}} \times 100 \% \\
=\mathbf{0 . 9 0 \%} \leq \mathbf{5} \%
\end{array}
$$

Therefore, approximation would be appropriate.

$$
\begin{aligned}
& \% \text { Dissociation }=\frac{\left\lfloor\mathrm{OH}^{-}\right\rfloor^{-}}{\left[\mathrm{CN}^{-}\right]_{0}} \times 100 \% \\
& \% \text { Dissociation }=\frac{0.0018 \mathrm{M}}{0.200 \mathrm{M}} \times 100 \%
\end{aligned}
$$

$\%$ Dissociation $=\mathbf{0 . 9 0 \%}$

$$
\begin{aligned}
& \mathrm{pH}=14-\mathrm{pOH} \\
& \mathrm{pH}=14-(2.75) \\
& \mathrm{pH}=\mathbf{1 1 . 2 5}
\end{aligned}
$$

$\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10^{-\mathrm{pH}}=10^{-11.25}$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=5.6 \times 10^{-12} \mathrm{M}$

## Assignment

16.6 \& 16.7 pg. 570 \#53 to 58; pg. 571 \#94

## 16.9: Acid-Base Properties of Salts

Salts: - ionic compounds that might dissociate in water.

1. Neutral Salts: - when the Cation comes from a Strong Base and the Anion is the Conjugate-Base of Strong Acid.

- no effect on $\mathbf{p H}$; if dissolve in pure water, $\mathbf{p H}$ will remain at 7 .

Examples: Some Neutral Salts:
a. $\mathrm{KNO}_{3(a q)}\left(\mathrm{K}^{+}\right.$can be from a strong base $-\mathrm{KOH}_{(a q)} ; \mathrm{NO}_{3}^{-}$is the conjugate-base of a strong acid $\left.-\mathrm{HNO}_{3(a q)}\right)$
b. $\mathrm{NaCl}_{(a q)}\left(\mathrm{Na}^{+}\right.$can be from a strong base $-\mathrm{NaOH}_{(a q)} ; \mathrm{Cl}^{-}$is the conjugate-base a strong acid $\left.\mathrm{HCl}_{(a q)}\right)$
2. Basic Salts: - when the Cation comes from a Strong Base and the Anion is the Conjugate-Base of a Weak Acid.

- $\overline{\mathrm{pH}}$ will increase; if dissolve in pure water, $\mathrm{pH}>7$ (Basic).

Examples: Some Basic Salts:
a. $\mathrm{NaCH}_{3} \mathrm{COO}_{(a q)}\left(\mathrm{Na}^{+}\right.$can be from a strong base $-\mathrm{NaOH}_{(a q)} ; \mathrm{CH}_{3} \mathrm{COO}^{-}$is the conjugate-base of a weak acid $\left.-\mathrm{CH}_{3} \mathrm{COOH}_{(a q)}\right)$
b. $\quad \mathrm{KF}_{(a q)}\left(\mathrm{K}^{+}\right.$can be from a strong base $-\mathrm{KOH}_{(a q)} ; \mathrm{F}^{-}$is the conjugate base of a weak acid $\left.-\mathrm{HF}(a q)\right)$

Hydrolysis: - the reaction of a base and a water to form a conjugate acid and $\mathrm{OH}^{-}$.

- it is basically the Brønsted-Lowry Dissociation of a weak base.

$$
\begin{array}{llll}
\mathbf{B}_{(a q)}+\mathbf{H}_{2} \mathbf{O}_{(l)} \rightleftharpoons \mathbf{O H}_{(a q)}^{-} & +\quad \mathrm{HB}_{(a q)}^{+} \\
\text {(Weak Base) } & (\text { Acid }) & (\text { Conjugate Base }) & (\text { Conjugate Acid) })
\end{array} \quad K_{b}=\frac{\left[\mathbf{O H}^{-} \mathbf{T} \mathbf{H B}^{+}\right]}{[\mathbf{B}]}
$$

Percent Hydrolysis: - the amount of $\left[\mathrm{OH}^{-}\right]$dissociated from the original $[\mathrm{B}]_{0}$ expressed in percentage.

- strong bases will have $\%$ Hydrolysis $=100 \%$.
- weak bases will have \% Hydrolysis < 100\%

$$
\begin{gathered}
\text { Percent Hydrolysis of Bases } \\
\% \text { Hydrolysis }=\frac{\left[\mathrm{OH}^{-}\right]}{[\mathrm{B}]_{0}} \times 100 \%
\end{gathered}
$$

3. Acidic Salts: - when the Cation is the Conjugate-Acid of a Weak Base and the Anion is the Conjugate-Base of a Strong Acid.
Example: $\mathrm{NH}_{4} \mathrm{ClO}_{4(a q)}$ is an acidic Salts: $\left(\mathrm{NH}_{4}{ }^{+}\right.$is the conjugate-acid of a weak base $-\mathrm{NH}_{3(a q)} ; \mathrm{ClO}_{4}{ }^{-}$is the conjugate-base of a strong acid $\left.-\mathrm{HClO}_{4}(a q)\right)$

Example 1: Determine the pH and the percent hydrolysis of 0.235 M of sodium nitrite. The acid dissociation constant for nitrous acid is $K_{a}=4.0 \times 10^{-4}$.
Sodium nitrite ( $\mathbf{N a N O}_{2}$ ) dissociates completely in $\mathbf{H}_{2} \mathbf{O}: \mathrm{NaNO}_{2(s)} \rightarrow \mathrm{Na}_{(a q)}^{+}+\mathrm{NO}_{2}^{-}{ }_{(a q)}$ (Weak Base)
Major Species: $\mathrm{NO}_{2}{ }^{-}{ }_{(a q)}, \mathrm{H}_{2} \mathrm{O}_{(l)}$

$$
K_{b}=\frac{K_{w}}{K_{a}}=\frac{1.00 \times 10^{-14}}{4.0 \times 10^{-4}} \quad K_{b}=2.5 \times 10^{-11}
$$

Strongest Base: $\mathbf{N O}_{\mathbf{2}}{ }^{-}\left(K_{b}=2.5 \times \mathbf{1 0}^{\mathbf{- 1 1}}\right) \quad\left(K_{b}\right.$ for $\mathrm{H}_{2} \mathrm{O}$ is $\left.K_{w}=1.0 \times 10^{-14}\right)$
$\mathbf{N O}_{2}{ }^{-}$is a weak base and undergoes Bronsted-Lowry Dissociation.

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

|  | $\left[\mathrm{NO}_{2}{ }^{-}\right]$ |  | $\left[\mathrm{HNO}_{2}\right]$ | $\left[\mathrm{OH}^{-}\right]$ |
| :--- | :---: | :---: | :---: | :---: |
| Initial | $\mathbf{0 . 2 3 5} \mathbf{~ M}$ | 0 |  |  |
| Change | $-x$ |  | 0 <br> $+x$ |  |
| Equilibrium | $(0.235-x)$ | $x$ | $x$ |  |

$$
\begin{aligned}
K_{b}=\frac{\left[\mathrm{HNO}_{2}\left[\mathrm{OH}^{-}\right]\right.}{\left[\mathrm{NO}_{2}^{-}\right]} 2.5 \times 10^{-11} & =\frac{(x)(x)}{(0.235-x)} \approx \frac{x^{2}}{(0.235)^{-}} \\
2.5 \times 10^{-11}(0.235) & \approx x^{2} \\
5.875 \times 10^{-12} & \approx x^{2} \\
x & \approx \sqrt{(0.235-x) \approx 0.235[x \text { is so small }} \begin{aligned}
\text { compared to } 0.235 \mathrm{M}]
\end{aligned} \\
\boldsymbol{x}=\left[\mathbf{O H}^{-}\right] & \approx \mathbf{2 . 4 \times 1 0 ^ { - 6 }} \mathbf{M}
\end{aligned}
$$

$$
\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right] \quad \mathrm{pH}=14-\mathrm{pOH}
$$

$$
\mathrm{pOH}=-\log \left(2.4 \times 10^{-6}\right) \quad \mathrm{pH}=14-(5.62)
$$

$$
\mathrm{pOH}=5.62
$$

$$
\mathrm{pH}=8.38
$$

$\%$ Hydrolysis $=\frac{\left[\mathbf{O H}^{-}\right]}{\left[\mathbf{N O}_{2}^{-}\right]_{0}} \times 100 \%=\frac{2.4 \times 10^{-6} \mathrm{M}}{0.235 \mathrm{M}} \times 100 \% \quad \%$ Hydrolysis $=\mathbf{0 . 0 0 1 0 2} \%$
As the small $K_{b}$ suggests, the $\left[\mathrm{OH}^{-}\right]$is very small compared to $\left[\mathrm{NO}_{2}{ }^{-}\right]_{0}$. Therefore, $\%$ hydrolysis is also verv small as a result.

Example 2: Determine the pH of 0.0750 M of ammonium nitrate. The base dissociation constant for $\mathrm{NH}_{3 \text { (aq) }}$ is $K_{b}=1.8 \times 10^{-5}$.
Ammonium nitrate, $\mathbf{N H}_{4} \mathbf{N O}_{3}$, dissociates completely in water:

$$
\begin{array}{ll}
\mathrm{NH}_{4} \mathrm{NO}_{3(s)} & \rightarrow \mathrm{NH}_{4}^{+}(a q) \\
0.0750 \mathrm{M} & 0.0750 \mathrm{M}
\end{array}
$$

Major Species: $\mathbf{N H}_{4}{ }^{+}{ }_{(a q)}, \mathbf{H}_{2} \mathbf{O}_{(I)}$

$$
K_{a}=\frac{K_{w}}{K_{b}}=\frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} \quad K_{a}=5.556 \times 10^{-10}
$$

Strongest Acid: $\mathrm{NH}_{4}{ }^{+}\left(K_{a}=\mathbf{5 . 5 5 6} \times \mathbf{1 0}^{\mathbf{- 1 0}}\right) \quad\left(K_{a}\right.$ for $\mathrm{H}_{2} \mathrm{O}$ is $\left.K_{w}=1.0 \times 10^{-14}\right)$ $\mathrm{NH}_{4}{ }^{+}$is a weak acid and undergoes Bronsted-Lowry Dissociation.

| $\mathrm{NH}_{4}{ }_{(a q)}+\mathrm{H}_{2} \mathrm{O}{ }_{(I)} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}{ }_{(a q)}+\mathrm{NH}_{3}(\mathrm{aq})$ |  |  |  |
| :---: | :---: | :---: | :---: |
|  | $\left[\mathrm{NH}_{4}^{+}{ }^{+}\right]$ | $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$ | [ $\mathrm{NH}_{3}$ ] |
| Initial | 0.0750 M | 0 | 0 |
| Change | - $\chi$ | + $X$ | + $X$ |
| Equilibrium | (0.075-x) | $x$ | $x$ |

## CAN use Approximation:

$$
\begin{aligned}
\frac{\left\lfloor\mathrm{NH}_{4}{ }^{+}\right\rfloor_{0}}{K_{a}} & =\frac{0.0750 \mathrm{M}}{5.556 \times 10^{-10}} \\
& =1.35 \times \mathbf{1 0}^{\mathbf{8}} \geq \mathbf{1 0 0 0}
\end{aligned}
$$

$$
\begin{aligned}
& K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{NH}_{3}\right]}{\left[\mathrm{NH}_{4}^{+}\right]} \\
& 5.556 \times 10^{-10}=\frac{(x)(x)}{(0.075-x)} \approx \frac{x^{2}}{(0.075)} \\
& 5.556 \times 10^{-10}(0.075) \approx x^{2} \\
& 4.167 \times 10^{-11} \approx x^{2} \\
& x \approx \sqrt{4.167 \times 10^{-11}} \\
& \text { se si } \\
& \text { se }=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \approx 6.455 \times 10^{-6} \mathrm{M} \\
& \mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \\
& \mathrm{pH}=-\log \left(6.455 \times 10^{-6}\right) \\
& \mathrm{pH}=\mathbf{5 . 1 9}
\end{aligned}
$$

## Verify for Using Approximation:

$$
\begin{aligned}
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] } \\
\left.\mathrm{NH}_{4}^{+}\right]_{0}
\end{aligned} r 100 \%=\frac{6.455 \times 10^{-6} \mathrm{M}}{0.0750 \mathrm{M}} \times 100 \% \mathrm{r} \quad \text { Therefore, approximation would be appropriate. }
$$

## Assignment

16.9 pg. 570-571 \#65, 68, 70 to 74

## Chapter 17: Acid-Base Equilibria

## 17.2: The Buffer Solutions

Buffered Solution: - a solution that resists a change in pH when a small amount of $\mathrm{H}_{3} \mathrm{O}^{+}$or $\mathrm{OH}^{-}$is added.

- consists of a pair of weak acid/conjugate base common ion or a pair of weak base/conjugate acid common ion.


## Acidic Buffered Solution:

$$
\begin{aligned}
& \mathbf{H A}_{(a q)}+\mathbf{H}_{2} \mathbf{O}_{(I)} \rightleftharpoons \mathbf{H}_{3} \mathbf{O}_{(a q)}^{+}+\mathbf{A}_{(a q)}^{-} \\
& \mathbf{A}_{(a q)}^{-}+\mathbf{H}_{3} \mathbf{O}_{(a q)}^{+} \rightarrow \mathbf{H}_{2} \mathbf{O}_{(l)}+\mathbf{H A}_{(a q)}
\end{aligned}
$$

$\left(\mathrm{H}^{+}\right.$- Strong Acid reacts completely with $\left.\mathbf{A}^{-}\right)$
(More HA - Weak Acid: pH will only be lowered SLIGHTLY!)
b. Small Amounts of $\mathbf{O H}^{-}$is Added:

$$
\mathrm{HA}_{(a q)}+\mathbf{O H}^{-}(a q) \rightarrow \mathbf{H}_{2} \mathrm{O}_{(l)}+\mathrm{A}_{(a q)}^{-}
$$

$$
\left(\mathrm{OH}^{-}\right. \text {- Strong Base reacts completely with HA) }
$$

(More $\mathrm{A}^{-}$- Weak Base: pH will only be raised SLIGHTLY!)
Basic Buffered Solution:

$$
\begin{gathered}
\mathbf{B}_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{(l)} \rightleftharpoons \mathrm{OH}^{-}(a q)+\mathrm{HB}^{+}{ }_{(a q)} \\
\mathbf{B}_{(a q)}+\mathrm{H}_{3} \mathrm{O}^{+}{ }_{(a q)} \rightarrow \mathrm{H}_{2} \mathrm{O}_{(I)}+\mathrm{HB}^{+}{ }_{(a q)}
\end{gathered}
$$

a. Small Amounts of $\mathrm{H}_{3} \mathrm{O}^{+}$is Added:
$\left(\mathrm{H}^{+}\right.$- Strong Acid reacts completely with B)
(More $\mathrm{HB}^{+}-$Weak Acid: pH will only be lowered SLIGHTLY!)
b. Small Amounts of $\mathrm{OH}^{-}$is Added:

$$
\mathbf{B}_{(a q)}+\mathbf{H}_{2} \mathrm{O}_{(l)} \rightleftharpoons \mathrm{OH}_{(a q)}^{-}+\mathrm{HB}_{(a q)}^{+}
$$

( $\mathrm{OH}^{-}$- Strong Base increases $\left[\mathrm{OH}^{-}\right]$; eq shifts left)
(More B - Weak Base: pH will only be raised SLIGHTLY!)
Example: $\mathrm{HCO}_{3}{ }^{-}{ }_{(a q)} / \mathrm{CO}_{3}{ }^{2-}$ is a buffer because $\mathrm{HCO}_{3}{ }^{-}$acts as an acid and $\mathrm{CO}_{3}{ }^{2-}$ acts as a base whenever a small amount of strong base or acid is added to it. Thus, pH will remain somewhat constant.
When small amounts of strong base is added: $\quad \mathrm{HCO}_{3}^{-}{ }_{(a q)}+\mathrm{OH}^{-}{ }_{(a q)} \rightarrow \mathrm{H}_{2} \mathrm{O}_{(l)}+\mathrm{CO}_{3}{ }^{2-}{ }_{(a q)}$
When small amounts of strong acid is added:
$\mathrm{CO}_{3}{ }^{2-}{ }_{(a q)}+\mathrm{H}_{3} \mathrm{O}^{+}{ }_{(a q)} \rightarrow \mathrm{H}_{2} \mathrm{O}_{(l)}+\mathrm{HCO}_{3}^{-}{ }_{(a q)}$
Example 1: Specify which of these systems can be classified as a buffer system.
a. $\mathrm{HNO}_{3} / \mathrm{KNO}_{3}$
b. $\mathrm{CH}_{3} \mathrm{COOH} / \mathrm{NaCH}_{3} \mathrm{COO}$
c. $\mathrm{H}_{2} \mathrm{SO}_{4} / \mathrm{NaHSO}_{4}$
d. $\mathrm{NH}_{3} / \mathrm{NH}_{4} \mathrm{Cl}$
$\mathrm{HNO}_{3}$ is a strong acid. Hence, $\mathrm{NO}_{3}{ }^{-}$is not a strong enough base to resist the change in $\mathrm{pH} . \mathrm{HNO}_{3}$ / $\mathrm{KNO}_{3}$ is $\underline{N O T}$ a buffer system.
$\mathrm{CH}_{3} \mathrm{COOH}$ is a weak acid.
Therefore, $\mathrm{CH}_{3} \mathrm{COO}^{-}$is a
strong enough weak base to
resist the change in pH .
$\mathrm{NaCH}_{3} \mathrm{COO}$ provides this
base. $\mathrm{CH}_{3} \mathrm{COOH} / \mathrm{CH}_{3} \mathrm{COO}^{-}$
is a buffer system.
$\mathrm{H}_{2} \mathrm{SO}_{4}$ is a strong acid. Hence, $\mathrm{HSO}_{4}{ }^{-}$ is not a strong enough base to resist the change in pH . $\mathrm{H}_{2} \mathrm{SO}_{4} / \mathrm{NaHSO}_{4}$ is NOT a buffer
$\mathrm{NH}_{3}$ is a weak base. Therefore, $\mathrm{NH}_{4}{ }^{+}$is a strong enough weak acid to resist the change in pH . $\mathrm{NH}_{4} \mathrm{Cl}$ provides this acid. $\mathbf{N H}_{\mathbf{3}} / \mathbf{N H}_{4} \mathbf{C l}$ is a buffer system.

Example 2: Calculate the pH of a 1.00 L buffered solution consisting of 0.500 M of methylamine $\left(K_{b}=4.38 \times 10^{-4}\right)$ with 0.450 M of $\mathrm{CH}_{3} \mathrm{NH}_{3} \mathrm{Cl}$ when:
a. 0.0200 mol of KOH is added to it.
b. 3.00 mL of 0.750 M of $\mathrm{HNO}_{3(a q)}$ is added to it.
c. Contrast the pH 's of the above two additions against the same additions to 1.00 L of water.

First, we have to figure out the $\left[\mathrm{OH}^{-}\right]$and $\mathbf{p H}$ for the buffered solution system.
Methylamine (Base) Dissociation: $\mathrm{CH}_{2} \mathrm{NH}_{2(a q)}+\mathrm{H}_{2} \mathrm{O}_{(I)} \rightleftharpoons \mathrm{CH}_{2} \mathrm{NH}_{3}{ }^{+}(a q)+\mathrm{OH}^{-}(a q)$
$\mathbf{C H}_{3} \mathbf{N H}_{3} \mathrm{Cl}$ : $\quad \mathrm{CH}_{3} \mathrm{NH}_{3} \mathrm{Cl}_{(a q)} \rightarrow \mathrm{CH}_{2} \mathrm{NH}_{3}{ }^{+}(a q)+\mathrm{Cl}^{-}{ }_{(a q)}$

$$
0.450 \mathrm{M} \quad \mathbf{0 . 4 5 0} \mathrm{M}
$$

$$
\mathrm{CH}_{2} \mathrm{NH}_{2}(a q)+\mathrm{H}_{2} \mathrm{O}_{(l)} \rightleftharpoons \mathrm{CH}_{2} \mathrm{NH}_{3}^{+}{ }_{(a q)}+\mathrm{OH}_{(a q)}^{-}
$$

|  | $\left[\mathrm{CH}_{2} \mathrm{NH}_{2}\right]$ | $\left[\mathrm{CH}_{2} \mathrm{NH}_{3}{ }^{+}\right]$ | $\left[\mathrm{OH}^{-}\right]$ |
| :--- | :---: | :---: | :---: |
| Initial | $\mathbf{0 . 5 0 0} \mathrm{M}$ | 0.450 M | 0 <br> $+x$ |
| Change | $-x$ | $+x$ | $+x$ |
| Equilibrium | $(0.5-x)$ | $(0.45+x)$ | $x$ |

$K_{b}=\frac{\left.\left[\mathrm{OH}^{-}\right] \mathrm{CH}_{2} \mathrm{NH}_{3}^{+}\right]}{\left[\mathrm{CH}_{2} \mathrm{NH}_{2}\right]} 4.38 \times 10^{-4}=\frac{(x)(0.45+x)}{(0.5-x)} \approx \frac{x(0.45)}{(0.5)}$

$$
4.38 \times 10^{-4} \frac{(0.5)}{(0.45)} \approx x
$$

Verify that we could use Approximation:

$$
x \approx 4.87 \times 10^{-4}
$$

CAN use Approximation:

$$
\begin{aligned}
\frac{\left[\mathrm{CH}_{2} \mathrm{NH}_{2}\right]_{0}}{K_{b}} & =\frac{0.500 \mathrm{M}}{4.38 \times 10^{-4}} \\
& =\mathbf{1 1 4 2} \mathbf{\geq 1 0 0 0}
\end{aligned}
$$

Use 0.45 in the numerator, because $(0.45+x) \approx 0.45$ [ $x$ is so small compared to 0.45 M$]$. Use 0.5 in the denominator, because $(0.5-x) \approx 0.5 \quad[x$ is so small compared to 0.5 M$]$.
a. 0.0200 mol of KOH is added to the buffered solution (Complete Run between $\mathbf{O H}^{-} \& \mathbf{C H}_{2} \mathbf{N H}_{3}{ }^{+}$).

|  | $\mathbf{O H}^{-}{ }_{(a q)}$ |  | $+\mathrm{CH}_{2} \mathrm{NH}_{3}{ }_{(a q)}$ |
| :--- | :---: | :---: | :---: | $\mathbf{H}_{2} \mathrm{O}_{(l)}+\mathbf{C H}_{\mathbf{2}} \mathbf{N H}_{2}(a q)$

Recalculate equilibrium concentrations using NEW $\left[\mathrm{CH}_{\mathbf{2}} \mathbf{N H}_{3}{ }^{+}\right]_{0}$ and $\left[\mathbf{C H}_{\mathbf{2}} \mathbf{N H}_{\mathbf{2}}\right]_{0}$

$$
\mathrm{CH}_{2} \mathrm{NH}_{2(a q)}+\mathrm{H}_{2} \mathrm{O}_{(l)} \rightleftharpoons \mathrm{CH}_{2} \mathrm{NH}_{3}{ }_{(a q)}+\mathrm{OH}_{(a q)}^{-}
$$

|  | $\left[\mathrm{CH}_{2} \mathbf{N H}_{2}\right]$ | $\left[\mathrm{CH}_{2} \mathrm{NH}_{3}{ }^{+}\right]$ | $\left[\mathrm{OH}^{-}\right]$ |
| :--- | :---: | :---: | :---: | :---: |
| Initial | $\mathbf{0 . 5 2 0} \mathbf{M}$ | 0.430 M | $\mathbf{0}$ |
| Change | $-\boldsymbol{y}$ | $+y$ | $+y$ |
| Equilibrium | $\mathbf{( 0 . 5 2 - y )}$ | $(0.43+y)$ | $\boldsymbol{y}$ |

$$
\begin{aligned}
& K_{b}=\frac{\left[\mathrm{OH}^{-}\right]\left[\mathrm{CH}_{2} \mathrm{NH}_{3}^{+}\right]}{\left[\mathrm{CH}_{2} \mathrm{NH}_{2}\right]} 4.38 \times 10^{-4} \approx \frac{y(0.43)^{-}}{(0.52)^{\longleftarrow}} \\
& 4.38 \times 10^{-4}=\frac{(y)(0.43+y)}{(0.52-y)} \\
& 4.38 \times 10^{-4} \frac{(0.52)}{(0.43)} \approx y
\end{aligned}
$$

$$
y \approx 5.30 \times 10^{-4}
$$

Verify that we could use Approximation:
$\frac{\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{CH}_{2} \mathrm{NH}_{2}\right]_{0}} \times 100 \%=\frac{5.30 \times 10^{-4} \mathrm{M}}{0.520 \mathrm{M}} \times 100 \%$
$=0.102 \% \leq 5 \%$ (Appropriate Approximation)
$\left[\mathrm{OH}^{-}\right]=5.30 \times 10^{-4} \mathbf{~ m o l} / \mathrm{L}$
$\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right]$
$\mathrm{pOH}=-\log \left(5.30 \times 10^{-4}\right)$

$$
\mathrm{pH}=14-\mathrm{pOH}
$$

$$
\mathrm{pH}=14-3.28
$$

$\mathrm{pOH}=3.28$

CAN use Approximation:
$\frac{\left[\mathrm{CH}_{2} \mathrm{NH}_{2}\right]_{0}}{K_{b}}=\frac{0.520 \mathrm{M}}{4.38 \times 10^{-4}}=\mathbf{1 1 8 7} \geq \mathbf{1 0 0 0}$
Use 0.43 in the numerator, because ( 0.43
$+y) \approx 0.43$ [ $y$ is so small compared to - 0.43 M$]$.

Use 0.52 in the denominator, because $(0.52-y) \approx 0.52[y$ is so small compared to 0.52 M$]$.

$$
\begin{aligned}
& \frac{\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{CH}_{2} \mathrm{NH}_{2}\right]_{0}} \times 100 \%=\frac{4.87 \times 10^{-4} \mathrm{M}}{0.500 \mathrm{M}} \times 100 \% \\
& {\left[\mathrm{OH}^{-}\right]=4.87 \times 10^{-4} \mathrm{~mol} / \mathrm{L}} \\
& =0.0973 \% \leq 5 \% \\
& \mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right] \\
& \mathrm{pOH}=-\log \left(4.87 \times 10^{-4}\right) \\
& \mathrm{pH}=14-\mathrm{pOH} \\
& \mathrm{pH}=14-3.31 \\
& \text { Therefore, approximation would be appropriate. } \\
& \mathrm{pOH}=3.31
\end{aligned}
$$

b. 3.00 mL of $0.750 \mathrm{M}(0.00225 \mathrm{~mol})$ of $\mathrm{HNO}_{3 \text { (aq) }}$ is added to the buffered solution (Complete Reaction between $\mathbf{H}_{3} \mathbf{O}^{+} \& \mathbf{C H}_{2} \mathbf{N H}_{2}$ ).


Recalculate equilibrium concentrations using NEW $\left[\mathbf{C H}_{2} \mathbf{N H}_{2}\right]_{0}$ and $\left[\mathrm{CH}_{2} \mathbf{N H}_{3}{ }^{+}\right]_{0}$ (neglect $\Delta$ volume)


CAN use Approximation:
$\frac{\left[\mathrm{CH}_{2} \mathrm{NH}_{2}\right]_{0}}{K_{b}}=\frac{0.520 \mathrm{M}}{4.38 \times 10^{-4}}=\mathbf{1 1 8 7} \geq \mathbf{1 0 0 0}$
Use 0.45225 in the numerator, because $(0.45225+z) \approx 0.45225$ [ $z$ is so small compared to 0.45225 M$]$.
Use 0.49775 in the denominator, because $(0.49775-z) \approx 0.49775$ [ $z$ is so small compared to 0.49775 M$]$.

Verify that we could use Approximation:

$$
\frac{\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{CH}_{2} \mathrm{NH}_{2}\right]_{0}} \times 100 \%=\frac{4.82 \times 10^{-4} \mathrm{M}}{0.49775 \mathrm{M}} \times 100 \%
$$

$$
\begin{array}{ll} 
& \left.\mathrm{OH}^{-}\right]=\mathbf{4 . 8 2} \times \mathbf{1 0}^{-4} \mathbf{~ m o l} / \mathrm{L} \\
& \mathrm{pH}=14-\mathrm{pOH} \\
& \mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right] \\
\mathrm{pOH}=-\log \left(4.82 \times 10^{-4}\right) & \mathrm{pH}=14-3.28 \\
\text { ion) } & \mathrm{pOH}=\mathbf{3 . 3 2}
\end{array}
$$

$=0.0968 \% \leq 5 \%$ (Appropriate Approximation)
c. Contrast the pH 's of the above two additions against the same additions to 1.00 L of water.
i. 0.0200 mol of KOH is added to 1.00 L of water

$$
\begin{array}{ll}
\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right] & \mathrm{pH}=14-\mathrm{pOH} \\
\mathrm{pOH}=-\log (0.0200) & \mathrm{pH}=14-1.70 \\
\mathbf{p O H}=\mathbf{1 . 7 0} & \mathbf{p H}=\mathbf{1 2 . 3 0}
\end{array}
$$

Adding the 0.0200 mol of KOH to buffered solution.

ii. 3.00 mL of $0.750 \mathrm{M}(0.00225 \mathrm{~mol})$ of $\mathrm{HNO}_{3(a q)}$ is added to 1.00 L of water (neglect $\Delta$ volume).
$\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$
$\mathrm{pH}=-\log (0.00225)$
$\mathrm{pH}=2.65$

Adding the 0.00225 mol of $\mathrm{HNO}_{3}$ to buffered solution.
pH changes from 10.69 to 10.68

## Assignment

17.2 pg. 604 \#1, 5 and 6

## 17.3: A Closer Look at Acid-Base Titrations

pH Curve: - a graph that shows the how the pH changes as the titration proceeds (as titrant is to the analyzed).

Titration: - a volumetric analysis that involves measuring the volume of known concentration solution to measure a given volume of an unknown concentration solution.

## Titration Set-up



> Titrant: - the solution of known concentration.
> Buret: - a precise apparatus to deliver the titrant.
> - the volume of the titrant added is read by subtracting the final volume and the initial volume.

Buret Valve: - can be adjusted to let one drop out at a time.

Erlenmeyer Flask: - a container commonly uses to hold the analyte. (Narrow mouth prevents splash and spillage.)

Acid-Base Titration: - volumetric analysis that assist in determining the unknown concentration in an acid and base neutralization.

Equivalent Point (Stoichiometric Point): - a point where the number of moles of $\mathrm{H}^{+}$is equivalent to the number of moles of $\mathrm{OH}^{-} .\left(n_{\mathrm{H}}{ }^{+}=\mathrm{nOH}_{\mathrm{OH}^{-}}\right)$

Endpoint: - a point where the indicator actually changes colour to indicate neutralization is completed.
Indicator: - a chemical that changes colour due to the pH of the solution (more in the next section).
Inflection: - the part of the curve where there is a sudden rise or drop in pH .

- the midpoint of the inflection marks the equivalence point.

1. Titration Between Strong Acids and Strong Base: - Equivalence Point always occur at $\mathbf{p H}=7$.

Strong Acid (unknown concentration with known volume - analyte) titrated with Strong

Base (known concentration - titrant)


Strong Base (unknown concentration and known volume - analyte) titrated with Strong Acid (known concentration - titrant)

Example 1: Calculate the pH when 30.0 mL of $0.100 \mathrm{M}^{\text {of }} \mathrm{HCl}_{(a q)}$ is titrated with 0.200 M of $\mathrm{KOH}_{(a q)}$ at:
a. 0 mL of $\mathrm{KOH}_{(a q)}$ added.
b. 5.00 mL of $\mathrm{KOH}_{(a q)}$ added.
c. 15.00 mL of $\mathrm{KOH}_{(a q)}$ added.
d. 20.00 mL of $\mathrm{KOH}_{(a q)}$ added.
a. At 0 mL of $\mathrm{KOH}_{(a q)}$ added, the pH will be solely based on the $[\mathrm{HCl}]$ in the flask:

$$
\mathrm{HCl}_{(a q)}+\mathbf{H}_{2} \mathrm{O}_{(l)} \rightarrow \mathrm{H}_{3} \mathrm{O}_{(a q)}^{+}+\mathrm{Cl}_{(a q)}^{-}
$$

$\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=-\log (0.100)$

```
pH=1.00
```

b. At 5.00 mL of $\mathrm{KOH}_{(a q)}$ added: (Before Stoichiometric Point)

|  | SA |  | $\left.\begin{array}{c}\mathrm{A} \\ \text { Chemical Species Present: } \\ \mathrm{H}_{3} \mathrm{O}^{+}, \mathrm{Cl}^{-}, \mathrm{K}^{+}, \\ \mathbf{O H}^{-}\end{array}, \begin{array}{c}\mathrm{H}_{2} \mathrm{O} \\ \mathrm{SB}\end{array}\right)$ |
| :---: | :---: | :---: | :---: |


| Net-Ionic | quation: $\quad \mathrm{H}_{3} \mathrm{O}^{+}(a q)$ | $\mathrm{OH}^{-}(a q) \quad \rightarrow \quad 2 \mathrm{H}_{2} \mathrm{O}_{(l)}$ |
| :---: | :---: | :---: |
|  | $n$ of $\mathrm{H}_{3} \mathrm{O}^{+}$ | $\boldsymbol{n}$ of $\mathbf{O H}^{-}$ |
| Before Change | $\begin{gathered} \hline(0.100 \mathrm{~mol} / \mathrm{L})(30.00 \mathrm{~mL})=3.00 \mathrm{mmol} \\ -\mathbf{1 . 0 0} \mathbf{~ m m o l} \end{gathered}$ | $\begin{gathered} (0.200 \mathrm{~mol} / \mathrm{L})(5.00 \mathrm{~mL})=1.00 \mathrm{mmol}(\mathrm{LR}) \\ -\mathbf{1 . 0 0} \mathbf{~ m m o l} \end{gathered}$ |
| After | 2.00 mmol | 0.00 mmol |

$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{n_{\mathrm{H}_{3} \mathrm{O}^{+}}}{\text {Total Volume }}=\frac{2.00 \mathrm{mmol}}{(30.00 \mathrm{~mL}+5.00 \mathrm{~mL})}=0.05714 \mathrm{~mol} / \mathrm{L}$
$\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=-\log (0.05714)$
( pH 's results from similar Calculations with other volumes before the
c. At 15.00 mL of $\mathrm{KOH}_{(a q)}$ added: (Stoichiometric Point)
SA A

Chemical Species Present: $\quad \mathrm{H}_{3} \mathrm{O}^{+}, \mathrm{Cl}^{-}, \mathrm{K}^{+}, \mathbf{O H}^{-}, \mathrm{H}_{2} \mathrm{O}$
B SB B

$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left[\mathrm{OH}^{-}\right]=1.00 \times 10^{-7} \mathrm{~mol} / \mathrm{L}$
$\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=-\log \left(1.00 \times 10^{-7}\right)$
$\mathrm{pH}=7.00$
d. At 20.00 mL of $\mathrm{KOH}_{(a q)}$ added: (After Stoichiometric Point)


Net-Ionic Equation:
$\mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{OH}^{-}$

|  | $n$ of $\mathrm{H}_{3} \mathrm{O}^{+}$ | $\boldsymbol{n}$ of $\mathbf{O H}^{-}$ |
| :---: | :---: | :---: |
| Before | $(0.100 \mathrm{~mol} / \mathrm{L})(30.00 \mathrm{~mL})=3.00 \mathrm{mmol}$ (Limiting Reagent) | $(0.200 \mathrm{~mol} / \mathrm{L})(20.00 \mathrm{~mL})=4.00 \mathrm{mmol}$ |
| Change | - 3.00 mmol | - 3.00 mmol |
| After | 0.00 mmol | 1.00 mmol |

$\left[\mathrm{OH}^{-}\right]=\frac{n_{\mathrm{OH}^{-}}}{\text {Total Volume }}=\frac{1.00 \mathrm{mmol}}{(30.00 \mathrm{~mL}+20.00 \mathrm{~mL})}=0.0200 \mathrm{~mol} / \mathrm{L}$

$$
\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right]=-\log (0.0200)
$$

$$
\mathrm{pOH}=1.70
$$

$$
\mathrm{pH}=14-\mathrm{pOH}
$$

( pH 's results from similar Calculations with other volumes after the
pH of 30.0 mL of $0.100 \mathrm{M} \mathrm{HCl}_{(a q)}$ titrated by $0.200 \mathrm{M} \mathrm{of} \mathrm{KOH}_{(a q)}$

| Volume of KOH added | $\mathbf{p H}$ | Volume of KOH added | $\mathbf{p H}$ | Volume of KOH <br> added | $\mathbf{p H}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 0.00 mL | 1.00 | 14.60 mL | 2.75 | 15.40 mL | 11.25 |
| 5.00 mL | 1.24 | 14.80 mL | 3.05 | 15.60 mL | 11.42 |
| 10.00 mL | 1.60 | 14.90 mL | 3.35 | 15.80 mL | 11.54 |
| 11.00 mL | 1.71 | 14.95 mL | 3.65 | 16.00 mL | 11.64 |
| 12.00 mL | 1.85 | 14.99 mL | 4.35 | 20.00 mL | 12.30 |
| 13.00 mL | 2.03 | $\mathbf{1 5 . 0 0} \mathbf{~ m L}(\mathbf{E q u i v a l e n c e )}$ | 7.00 | 25.00 mL | 12.56 |
| 14.00 mL | 2.34 | 15.01 mL | 9.65 | 30.00 mL | 12.70 |
| 14.20 mL | 2.44 | 15.05 mL | 10.35 | 35.00 mL | 12.79 |
| 14.40 mL | 2.57 | 15.20 mL | 10.95 |  |  |

pH of 30.0 mL of 0.100 M HCl titrated by 0.200 M of KOH

2. Titration Between Weak Acids and Strong Base: - Equivalence Point always occur at pH $>7$.

Weak Acid (unknown concentration with known volume - analyte) titrated with


Example 2: Calculate the pH when 30.0 mL of 0.100 M of $\mathrm{HCOOH}_{(a q)}\left(K_{a}=1.8 \times 10^{-4}\right)$ is titrated with $0.200 \mathrm{~mol} / \mathrm{L}^{\text {of }} \mathrm{KOH}_{(a q)}$ at:
a. 0 mL of $\mathrm{KOH}_{(a q)}$ added.
b. 7.50 mL of $\mathrm{KOH}_{(a q)}$ added.
c. 15.00 mL of $\mathrm{KOH}_{(a q)}$ added.
d. 20.00 mL of $\mathrm{KOH}_{(a q)}$ added.
a. At 0 mL of $\mathrm{KOH}_{(a q)}$ added, the pH will be calculated the weak acid dissociation in the flask:

$$
\mathrm{HCOOH}_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{(l)} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}_{(a q)}^{+}+\mathrm{HCOO}_{(a q)}^{-}
$$

CANNOT use Approximation:

|  | $[\mathrm{HCOOH}]$ |  | $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$ | $\left[\mathrm{HCOO}^{-}\right]$ |
| :--- | :---: | :---: | :---: | :---: |
| Initial | 0.100 M | 0 | 0 M |  |
| Change | $-x$ |  |  |  |

$$
\begin{aligned}
\frac{[\mathrm{HCOOH}]_{0}}{K_{a}} & =\frac{0.100 \mathrm{M}}{1.8 \times 10^{-4}} \\
& =\mathbf{5 5 5 . 6}<\mathbf{1 0 0 0}
\end{aligned}
$$

$K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{HCOO}^{-}\right]}{[\mathrm{HCOOH}]} \quad 1.8 \times 10^{-4}=\frac{(x)(x)}{(0.1-x)}=\frac{x^{2}}{(0.1-x)}$

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=x=0.0042 \mathrm{~mol} / \mathrm{L}
$$

$\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=-\log (0.042)$
$\mathrm{pH}=2.38$
b. At 7.50 mL of $\mathrm{KOH}_{(a q)}$ added: (Before Stoichiometric Point: at Halfway to Equivalence Point) Chemical Species Present: $\quad \mathbf{H C O O H}, \mathrm{K}^{+}, \mathrm{OH}^{-}, \mathrm{H}_{2} \mathrm{O}$

$$
\text { SA } \quad \text { SB } \quad \text { A/B }
$$

Net-Ionic Equation: $\mathrm{HCOOH}_{(a q)}+\quad \mathrm{OH}_{(a q)}^{-} \rightarrow \mathrm{H}_{2} \mathrm{O}_{(l)}+\mathrm{HCOO}_{(a q)}^{-}$

|  | $\boldsymbol{n}$ of $\mathbf{H C O O H}$ | $\boldsymbol{n}$ of $\mathbf{O H}^{-}$ | $\boldsymbol{n}$ of $\mathbf{H C O O}^{-}$ |
| :--- | :---: | :---: | :---: |
| Before | $(0.100 \mathrm{~mol} / \mathrm{L})(30.00 \mathrm{~mL})$ | $(0.200 \mathrm{~mol} / \mathrm{L})(7.50 \mathrm{~mL})$ | 0 mmol |
|  | $=3.00 \mathrm{mmol}$ | $=1.50 \mathrm{mmol}(\mathrm{LR})$ |  |
| Change | $-\mathbf{1 . 5 0 \mathrm { mmol }}$ | $-\mathbf{1 . 5 0 \mathbf { m m o l }}$ | $+\mathbf{1 . 5 0} \mathbf{~ m m o l}$ |
| After | $\mathbf{1 . 5 0} \mathbf{~ m m o l}$ | $\mathbf{0} \mathbf{~ m m o l}$ | $\mathbf{1 . 5 0} \mathbf{~ m m o l}$ |

$$
[\mathrm{HCOOH}]=\frac{n_{\text {HCOOH }}}{\text { Total Volume }}=\frac{1.50 \mathrm{mmol}}{(30.00 \mathrm{~mL}+7.50 \mathrm{~mL})}=0.0400 \mathrm{~mol} / \mathrm{L}, ~ \begin{gathered}
\\
{[\mathrm{HCOOH}]=\left[\mathrm{HCOO}^{-}\right]} \\
n_{\mathrm{HCOO}^{-}}- \\
\mathbf{p H} \approx \mathbf{p} \boldsymbol{K}_{a}
\end{gathered}
$$

$$
\left[\mathrm{HCOO}^{-}\right]=\frac{\mathrm{HCOO}^{-}}{\text {Total Volume }}=\frac{1.50 \mathrm{mmol}}{(30.00 \mathrm{~mL}+7.50 \mathrm{~mL})}=0.0400 \mathrm{~mol} / \mathrm{L} \quad \text { (Max Buffer Capacity) }
$$

After all the $\mathrm{OH}^{-}$is used up, the resulting solution follows the regular weak acid dissociation.

|  | $\mathrm{HCOOH}_{(a q)}+\mathrm{H}_{2} \mathrm{O}{ }_{(l)} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{HCOO}^{-}(a q)$ |  |  |
| :---: | :---: | :---: | :---: |
|  | [ HCOOH ] | $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$ | $\left[\mathrm{HCOO}^{-}\right]$ |
| Initial | 0.0400 M | 0 | $\mathbf{0 . 0 4 0 0 ~ M ~}$ |
| Change | - $X$ | + $x$ | $+x$ |
| Equilibrium | (0.04-x) | $x$ | (0.04 + x) |

$K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{HCOO}^{-}\right]}{[\mathrm{HCOOH}]} \quad 1.8 \times 10^{-4}=\frac{(x)(0.04+x)}{(0.04-x)}$
$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\boldsymbol{x}=\mathbf{1 . 8} \times \mathbf{1 0}^{-4} \mathbf{~ m o l} / \mathbf{L} \quad \mathrm{pH}=\mathrm{p} K_{a}=-\log \left(1.8 \times 10^{-4}\right)$
( pH 's results from similar Calculations with other volumes before the stoichiometric point is listed on page 306.)

CANNOT use Approximation:

$$
\begin{aligned}
\frac{[\mathrm{HCOOH}]_{0}}{K_{a}} & =\frac{0.0400 \mathrm{M}}{1.8 \times 10^{-4}} \\
& =\mathbf{2 2 2 . 2 2}<\mathbf{1 0 0 0}
\end{aligned}
$$


(0, $94-8-1 \cdot 8 \mathrm{E}-4$,
1.784 $15157 \mathrm{E}-4$
$\mathrm{pH}=3.75$
c. At 15.00 mL of $\mathrm{KOH}_{(a q)}$ added: (Stoichiometric Point)

Chemical Species Present: $\quad \mathbf{H C O O H}, \mathrm{K}^{+}, \mathbf{O H}^{-}, \mathrm{H}_{2} \mathrm{O}$
SA SB A/B

$\left[\mathrm{HCOO}^{-}\right]=\frac{n_{\mathrm{HCOO}^{-}}}{\text {Total Volume }}=\frac{3.00 \mathrm{mmol}}{(30.00 \mathrm{~mL}+15.00 \mathrm{~mL})}=0.0667 \mathrm{~mol} / \mathrm{L}$
At Stoichiometric Point, after all the $\mathrm{OH}^{-}$and HCOOH are used up, the resulting solution follows the regular weak base dissociation.


## CAN use Approximation:

$$
\begin{aligned}
\frac{\left[\mathrm{HCOO}^{-}\right]_{0}}{K_{b}} & =\frac{0.0667 \mathrm{M}}{5.556 \times 10^{-11}} \\
& =\mathbf{1 . 2 \times 1 0 ^ { 9 } \geq \mathbf { 1 0 0 0 }}
\end{aligned}
$$

$K_{b}=\frac{K_{w}}{K_{a}}=\frac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}} \quad K_{b}=5.556 \times 10^{-11}=\frac{[\mathrm{HCOOH}]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{HCOO}^{-}\right]}$ Use 0.0667 in the denominator, because $(0.0667-x) \approx 0.03667 \quad[x$ is so small compared to 0.0667 M$]$.

$$
5.556 \times 10^{-11}=\frac{(x)(x)}{(0.0667-x)} \approx \frac{x^{2}}{0.0667}
$$

$\left[\mathrm{OH}^{-}\right]=x=1.92 \times 10^{-6} \mathrm{~mol} / \mathrm{L}$
$\mathrm{pOH}=-\log \left(1.92 \times 10^{-6}\right)=5.72$
$\mathrm{pH}=14-\mathrm{pOH}=14-5.72$
d. At 20.00 mL of $\mathrm{KOH}_{(a q)}$ added: (After Stoichiometric Point)

Chemical Species Present: $\quad \mathrm{HCOOH}, \mathrm{K}^{+}, \mathrm{OH}^{-}, \mathrm{H}_{2} \mathrm{O}$

$$
\text { SA } \quad \text { SB } \quad \text { A/B }
$$

Net-Ionic Equation: $\mathrm{HCOOH}_{(a q)}+\quad \mathrm{OH}_{(a q)}^{-} \rightarrow \mathbf{H}_{2} \mathrm{O}_{(l)}+\mathrm{HCOO}_{(a q)}^{-}$

|  | $\boldsymbol{n}$ of $\mathbf{H C O O H}$ | $\boldsymbol{n}$ of $\mathbf{O H}^{-}$ |
| :--- | :---: | :---: |
| Before | $(0.100 \mathrm{~mol} / \mathrm{L})(30.00 \mathrm{~mL})$ | $(0.200 \mathrm{~mol} / \mathrm{L})(20.00 \mathrm{~mL})$ |
|  | $=3.00 \mathrm{mmol}(\mathrm{LR})$ | $=4.00 \mathrm{mmol}$ |
| Change | -3.00 mmol | $\mathbf{- 3 . 0 0} \mathbf{~ m m o l}$ |
| After | $\mathbf{0} \mathbf{~ m m o l}$ | $\mathbf{1 . 0 0} \mathbf{~ m m o l}$ |

After all the HCOOH is used up, the resulting solution has the following major species.
Chemical Species Present: $\quad \begin{aligned} & \mathrm{K}^{+}, \\ & \\ & \\ & \mathbf{O H}\end{aligned} \mathbf{O H}^{-}, \begin{gathered}\mathrm{H}_{2} \mathrm{O} \\ \mathrm{A} / \mathrm{B}\end{gathered}$
$\left[\mathrm{OH}^{-}\right]=\frac{n_{\mathrm{OH}^{-}}}{\text {Total Volume }}=\frac{1.00 \mathrm{mmol}}{(30.00 \mathrm{~mL}+20.00 \mathrm{~mL})}=0.0200 \mathrm{~mol} / \mathrm{L}$

$$
\mathrm{pH}=14-\mathrm{pOH}=14-1.70
$$

$$
\mathrm{pOH}=-\log (0.0200)=1.70
$$

$$
\mathrm{pH}=12.30
$$

( pH 's results from similar Calculations with other volumes after the stoichiometric point is listed on the next page.)
pH of 30.0 mL of $0.100 \mathrm{M} \mathrm{HCOOH}_{(a q)}$ titrated by $0.200 \mathrm{M} \mathrm{of} \mathrm{KOH}_{(a q)}$

| Volume of KOH added | $\mathbf{p H}$ | Volume of KOH added | $\mathbf{p H}$ | Volume of KOH added | $\mathbf{p H}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 0.00 mL | 2.38 | 14.40 mL | 5.13 | 15.20 mL | 10.95 |
| 5.00 mL | 3.45 | 14.60 mL | 5.31 | 15.40 mL | 11.25 |
| 7.50 mL (Halfway to Equivalence) | 3.75 | 14.80 mL | 5.62 | 15.60 mL | 11.42 |
| 10.00 mL | 4.05 | 14.90 mL | 5.91 | 15.80 mL | 11.54 |
| 11.00 mL | 4.19 | 14.95 mL | 6.22 | 16.00 mL | 11.64 |
| 12.00 mL | 4.35 | 14.99 mL | 6.92 | 20.00 mL | 12.30 |
| 13.00 mL | 4.56 | $\mathbf{1 5 . 0 0} \mathbf{~ m L}(\mathbf{E q u i v a l e n c e )}$ | 8.28 | 25.00 mL | 12.56 |
| 14.00 mL | 4.89 | 15.01 mL | 9.65 | 30.00 mL | 12.70 |
| 14.20 mL | 5.00 | 15.05 mL | 10.35 | 35.00 mL | 12.79 |

pH of 30.0 mL of 0.100 M HCOOH titrated by 0.200 M of KOH

3. Titration Between Weak Bases and Strong Acid: - Equivalence Point always occur at $\mathbf{p H}<7$.

Weak Base (unknown concentration with known volume - analyte) titrated with


Volume of Acid Added (mL)

Example 3: Calculate the pH when 30.0 mL of 0.100 M of $\mathrm{CH}_{3} \mathrm{NH}_{2(a q)}\left(K_{b}=4.38 \times 10^{-4}\right)$ is titrated with $0.200 \mathrm{~mol} / \mathrm{L}$ of $\mathrm{HCl}_{(a q)}$ at:
a. 0 mL of $\mathrm{HCl}_{(a q)}$ added.
b. 7.50 mL of $\mathrm{HCl}_{(a q)}$ added.
c. 15.00 mL of $\mathrm{HCl}_{(a q)}$ added.
d. 20.00 mL of $\mathrm{HCl}_{(a q)}$ added.
a. At 0 mL of $\mathrm{HCl}_{(a q)}$ added, the pH will be calculated the weak base dissociation in the flask:

|  | $\mathrm{CH}_{3} \mathbf{N H}_{2(a q)}+\mathrm{H}_{2} \mathrm{O}{ }_{(l)} \rightleftharpoons \mathrm{CH}_{3} \mathrm{NH}_{3}{ }_{(a q)}+\mathrm{OH}^{-}{ }_{(a q)}$ |  |  |
| :---: | :---: | :---: | :---: |
|  | [ $\mathrm{CH}_{3} \mathrm{NH}_{2}$ ] | $\left[\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right]$ | [ $\mathrm{OH}^{-}$] |
| Initial | 0.100 M | 0 | 0 M |
| Change | - $X$ | $+x$ | + $\boldsymbol{X}$ |
| Equilibrium | (0.1-x) | $X$ | $x$ |

CANNOT use Approximation:

$$
\begin{aligned}
\frac{\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right]_{0}}{K_{b}} & =\frac{0.100 \mathrm{M}}{4.38 \times 10^{-4}} \\
& =\mathbf{2 2 8 . 3}<\mathbf{1 0 0 0}
\end{aligned}
$$

$K_{b}=\frac{\left[\mathrm{CH}_{3} \mathrm{NH}_{3}^{+}\left[\mathrm{OH}^{-}\right]\right.}{\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right]}$

$$
4.38 \times 10^{-4}=\frac{(x)(x)}{(0.1-x)}=\frac{x^{2}}{(0.1-x)}
$$

$$
\left[\mathrm{OH}^{-}\right]=x=0.00640 \mathrm{~mol} / \mathrm{L}
$$

Solve( $\mathrm{K}_{2}(0,1-\mathrm{X})$ $-4,68 \mathrm{E}-4,8,0,60$, -1. 13
. 6164627793

$$
\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right]=-\log (0.00640)=2.19
$$

$$
\mathrm{pH}=14-\mathrm{pOH}=14-2.19
$$


b. At 7.50 mL of $\mathrm{HCl}_{(a q)}$ added: (Before Stoichiometric Point: at Halfway to Equivalence Point)

Chemical Species Present: $\quad \mathbf{C H}_{3} \mathbf{N H}_{3}, \mathbf{H}_{3} \mathbf{O}^{+}, \mathrm{Cl}^{-}, \mathrm{H}_{2} \mathrm{O}$
SB SA A/B

| Net-Ionic | tion: $\mathrm{CH}_{3} \mathrm{NH}_{2}(\mathrm{aq})$ | ${ }^{\text {a }}$ | $\rightarrow$ | $\frac{\mathrm{H}_{2} \mathrm{O}_{(l)}+\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}(a q)}{n \text { of } \mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}}$ |
| :---: | :---: | :---: | :---: | :---: |
|  | $\boldsymbol{n}$ of $\mathrm{CH}_{3} \mathrm{NH}_{2}$ | $n$ of $\mathrm{H}_{3} \mathrm{O}^{+}$ |  |  |
| Before | $(0.100 \mathrm{~mol} / \mathrm{L})(30.00 \mathrm{~mL})$ | ( $0.200 \mathrm{~mol} / \mathrm{L}$ ) $(7.50 \mathrm{~mL})$ |  | 0 mmol |
|  | $=3.00 \mathrm{mmol}$ | $=1.50 \mathrm{mmol}$ (LR) |  |  |
| Change | - 1.50 mmol | - 1.50 mmol |  | + 1.50 mmol |
| After | 1.50 mmol | 0 mmol |  | 1.50 mmol |

$\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right]=\frac{n_{\mathrm{CH}_{3} \mathrm{NH}_{2}}}{\text { Total Volume }}=\frac{1.50 \mathrm{mmol}}{(30.00 \mathrm{~mL}+7.50 \mathrm{~mL})}=0.0400 \mathrm{~mol} / \mathrm{L}$
$\left[\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right]=\frac{n_{\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}}^{\text {Total Volume }}=\frac{1.50 \mathrm{mmol}}{(30.00 \mathrm{~mL}+7.50 \mathrm{~mL})}=0.0400 \mathrm{~mol} / \mathrm{L}}{}=\begin{gathered}{\left[\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right]=\left[\mathrm{CH}_{2} \mathrm{NH}_{2}\right]} \\ \mathrm{pH} \approx \mathbf{p} K_{a} \\ (\text { Max Buffer Capacity })\end{gathered}$
After all the $\mathrm{H}_{3} \mathrm{O}^{+}$is used up, the resulting solution follows the regular weak base dissociation.

|  | $\mathrm{CH}_{3} \mathrm{NH}_{2(a q)}+\mathrm{H}_{2} \mathrm{O}(1) \rightleftharpoons \mathrm{CH}_{3} \mathrm{NH}_{3}{ }_{(a q)}+\mathrm{OH}^{-}{ }_{(a q)}$ |  |  |
| :---: | :---: | :---: | :---: |
|  | $\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right]$ | $\left[\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right]$ | $\left[\mathrm{OH}^{-}\right]$ |
| Initial | 0.0400 M | 0 | 0.0400 M |
| Change | -X | + $x$ | + $\boldsymbol{X}$ |
| Equilibrium | (0.04-x) | $x$ | (0.04+x) |

CANNOT use Approximation:

$$
\begin{aligned}
\frac{\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right]_{0}}{K_{b}} & =\frac{0.0400 \mathrm{M}}{4.38 \times 10^{-4}} \\
& =\mathbf{9 1 . 3}<\mathbf{1 0 0 0}
\end{aligned}
$$

$K_{b}=\frac{\left[\mathrm{CH}_{3} \mathrm{NH}_{3}^{+} \llbracket \mathrm{OH}^{-}\right]}{\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right]}$
$4.38 \times 10^{-4}=\frac{(x)(0.04+x)}{(0.04-x)}$
$\left[\mathrm{OH}^{-}\right]=x=4.29 \times 10^{-4} \mathrm{~mol} / \mathrm{L}$

(0, 04, $0,4,3 \mathrm{E}-4$
$4.287167932 \mathrm{E}-4$ $\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right]=-\log \left(4.29 \times 10^{-4}\right)=3.37$
$\mathrm{pH}=14-\mathrm{pOH}=14-3.37$
( pH 's results from similar Calculations with other volumes before the stoichiometric point is listed on the next page.)
c. At 15.00 mL of $\mathrm{HCl}_{(a q)}$ added: (Stoichiometric Point)

Chemical Species Present: $\quad \mathbf{C H}_{\mathbf{3}} \mathbf{N H}_{\mathbf{2}}, \mathbf{H}_{\mathbf{3}} \mathrm{O}^{+}, \mathrm{Cl}^{-}, \mathrm{H}_{2} \mathrm{O}$
SB SA A/B

$\left[\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right]=\frac{n_{\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}}}{\text {Total Volume }}=\frac{3.00 \mathrm{mmol}}{(30.00 \mathrm{~mL}+15.00 \mathrm{~mL})}=0.0667 \mathrm{~mol} / \mathrm{L}$

At Stoichiometric Point, after all the $\mathrm{H}_{3} \mathrm{O}^{+}$and $\mathrm{CH}_{3} \mathrm{NH}_{2}$ are used up, the resulting solution follows the regular weak acid dissociation.

|  | $\mathrm{CH}_{3} \mathrm{NH}_{3}{ }_{(a q)}^{+}+\mathrm{H}_{2} \mathrm{O}{ }_{(l)} \rightleftharpoons \mathrm{CH}_{3} \mathrm{NH}_{2(a q)}+\mathrm{H}_{3} \mathrm{O}^{+}{ }_{(a q)}$ |  |  |
| :---: | :---: | :---: | :---: |
|  | $\left[\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}\right]$ | $\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right]$ | $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$ |
| Initial | 0.0667 M | 0 | 0 M |
| Change | -x | + $X$ | $+x$ |
| Equilibrium | (0.0667-x) | $x$ | $x$ |

$K_{a}=\frac{K_{w}}{K_{b}}=\frac{1.0 \times 10^{-14}}{4.38 \times 10^{-4}} \quad K_{a}=2.28 \times 10^{-11}=\frac{\left[\mathrm{CH}_{2} \mathrm{NH}_{2}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{CH}_{3} \mathrm{NH}_{3}\right]}$

CAN use Approximation:

$$
\begin{aligned}
\frac{\left[\mathrm{CH}_{3} \mathrm{NH}_{3}^{+}\right]_{0}}{K_{a}} & =\frac{0.0667 \mathrm{M}}{2.28 \times 10^{-11}} \\
& =\mathbf{2 . 9 \times 1 0 ^ { 9 } \geq \mathbf { 1 0 0 0 }}
\end{aligned}
$$

Use 0.0667 in the denominator,
because $(0.0667-x) \approx 0.03667 \quad[x$ is so small compared to 0.0667 M ].

$$
2.28 \times 10^{-11}=\frac{(x)(x)}{(0.0667-x)} \approx \frac{x^{2}}{0.0667}
$$



$$
\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=-\log \left(1.23 \times 10^{-6}\right)
$$

$\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\boldsymbol{x}=\mathbf{1 . 2 3} \times \mathbf{1 0}^{-6} \mathbf{~ m o l} / \mathbf{L} \quad \mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=-\log \left(1.23 \times 10^{-6}\right)$

$$
\mathrm{pH}=5.91
$$

d. At 20.00 mL of $\mathrm{HCl}_{(a q)}$ added: (After Stoichiometric Point)

Chemical Species Present: $\quad \mathbf{C H}_{\mathbf{3}} \mathbf{N H}_{\mathbf{2}}, \mathbf{H}_{3} \mathbf{O}^{+}, \mathrm{Cl}^{-}, \mathrm{H}_{2} \mathrm{O}$

$$
\text { SB } \quad \text { SA } \quad \text { A/B }
$$

$\begin{aligned} & \text { Net-Ionic Equation: } \mathbf{C H}_{3} \mathbf{N H}_{\mathbf{2}(a q)}+\quad \mathbf{H}_{3} \mathbf{O}^{+}{ }_{(a q)} \rightarrow\end{aligned} \mathbf{H}_{2} \mathbf{H}_{2} \mathbf{O}_{(l)}+\mathbf{C H}_{3} \mathbf{N H}_{3}{ }^{+}(a q)$
After all the $\mathrm{CH}_{3} \mathrm{NH}_{2}$ is used up, the resulting solution has the following major species.
Chemical Species Present: $\quad \mathrm{Cl}^{-}, \underset{\mathrm{SA}}{\mathrm{H}_{3} \mathrm{O}^{+},} \xrightarrow[\mathrm{A} / \mathrm{B}]{\mathrm{H}_{2} \mathrm{O}}$

$$
\begin{aligned}
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] } & =\frac{n_{\mathrm{H}_{3} \mathrm{O}^{+}}}{\text {Total Volume }}=\frac{1.00 \mathrm{mmol}}{(30.00 \mathrm{~mL}+20.00 \mathrm{~mL})}=0.0200 \mathrm{~mol} / \mathrm{L} \\
\mathrm{pH} & =-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=-\log (0.0200)
\end{aligned}
$$

(pH's results from similar Calculations with other volumes after the stoichiometric point is listed below.)
pH of 30.0 mL of $0.100 \mathrm{M} \mathrm{CH}_{3} \underline{\mathrm{NH}}_{2(a q)}$ titrated by $0.200 \mathrm{M}^{\text {of } \mathrm{HCl}_{(a q)}}$

| Volume of HCL added | $\mathbf{p H}$ | Volume of $\mathbf{H C l}$ added | $\mathbf{p H}$ | Volume of HCl added | $\mathbf{p H}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 0.00 mL | 11.81 | 14.40 mL | 9.26 | 15.20 mL | 3.05 |
| 5.00 mL | 10.92 | 14.60 mL | 9.08 | 15.40 mL | 2.75 |
| 7.50 mL (Halfway to Equivalence) | 10.63 | 14.80 mL | 8.77 | 15.60 mL | 2.58 |
| 10.00 mL | 10.33 | 14.90 mL | 8.47 | 15.80 mL | 2.46 |
| 11.00 mL | 10.20 | 14.95 mL | 8.16 | 16.00 mL | 2.36 |
| 12.00 mL | 10.03 | 14.99 mL | 7.46 | 20.00 mL | 1.70 |
| 13.00 mL | 9.82 | $\mathbf{1 5 . 0 0} \mathbf{~ m L}(\mathbf{E q u i v a l e n c e})$ | $\mathbf{5 . 9 1}$ | 25.00 mL | 1.40 |
| 14.00 mL | 9.49 | 15.01 mL | 4.35 | 30.00 mL | 1.30 |
| 14.20 mL | 9.39 | 15.05 mL | 3.65 | 35.00 mL | 1.21 |

pH of 30.0 mL of 0.100 M Methylamine titrated by 0.200 M of HCI

4. Titration Between Strong Acid/Bases and Polyprotic Acid/Base: - there are multiple equivalence points. - the last equivalence point indicates the stoichiometric volume.


Copyrighted by Gabriel Tang B.Ed., B.Sc.

Example 4: Calculate the concentration of $10.00 \mathrm{~mL}^{\text {of }} \mathrm{Na}_{2} \mathrm{~S}_{(a q)}$ is titrated with 0.0350 M of $\mathrm{HBr}_{(a q)}$ when the first and second equivalence points are at 13.34 mL and 27.88 mL respectively.

For Acid-Base Stoichiometry, do NOT write the Net-Ionic Equation. Write the Molecular Equation to do Stoichiometry. We use the second equivalence point because $\mathrm{Na}_{2} \mathrm{~S}$ can accept two protons.

$$
\begin{array}{clllll}
2 \mathrm{HBr}_{(a q)} & + & \mathrm{Na}_{2} \mathrm{~S}_{(a q)} & \rightarrow & \mathrm{H}_{2} \mathrm{~S}_{(a q)} & + \\
27.88 \mathrm{~mL} & & 10.0 \mathrm{~mL} & & & \\
0.0350 \mathrm{~mol} / \mathrm{L} & & ? \mathrm{~mol} / \mathrm{L} & & & \\
\end{array}
$$

(1) $n_{\mathrm{HBr}}=C V=(0.0350 \mathrm{~mol} / \pm)(27.88 \mathrm{~mL})=0.9758 \mathrm{mmol}$
(2) $n_{\mathrm{Na}_{2} \mathrm{~s}}=0.9758 \mathrm{mmol} \mathrm{HBr} \times \frac{1 \mathrm{~mol} \mathrm{Na}_{2} \mathrm{~S}}{2 \mathrm{mel} \mathrm{HBr}}=0.4879 \mathrm{mmol} \mathrm{Na}_{2} \mathrm{~S}$
(3) $\left[\mathrm{Na}_{2} \mathrm{~S}\right]=\frac{n}{V}=\frac{0.4879 \mathrm{mmol}}{10.0 \mathrm{~mL}}=0.04879 \mathrm{~mol} / \mathrm{L}$


## Neutralization Reactions Between Weak Acids and Weak Bases

1. The reaction is NOT one way, but in equilibrium.
2. When writing out the equilibrium system, list all major species first (Do NOT Break up any Weak Acids and Weak Bases). Then, reacts the Strongest Acid (SA - donates a proton) and the Strongest Base ( SB - accepts a proton) from the list.
3. Using the Table of the Relative Strengths of Acids, decide on which side of the equilibrium is the system favoured. (The equilibrium favours the side with the Weakest Acid (Lower K ${ }_{\underline{g}}$ ) - because the stronger acid of the other side dissociates more.)

| Weak Acid and Weak Base Neutralization |
| :---: |
| $\underset{(\text { Stronger Acid })}{\mathbf{H A}_{(a q)}+\mathbf{B}_{(a q)} \rightleftharpoons \mathbf{A}_{(a q)}^{-}+\mathbf{H B}_{(a q)}^{+}} \underset{(\underline{\text { Weaker Acid) })}}{ }$ |
| $\mathbf{H} \mathbf{X}_{(a q)}+\mathbf{Y}_{(a q)} \rightleftharpoons \mathbf{X}_{(a q)}^{-}+\mathbf{H} \mathbf{Y}_{(a q)}^{+}$ <br> (Weaker Acid) (Stronger Acid) |

Example 5: Write the net-ionic equation for the following neutralizations. Indicate the side of the equilibrium system that is favoured.
a. Acetic Acid reacts with Ammonia

SA A
Chemical Species Present: $\mathrm{CH}_{3} \mathbf{C O O H}, \mathbf{N H}_{3}, \mathrm{H}_{2} \mathrm{O}$
SB B
Favour Products
Net-Ionic Equation: $\quad \mathrm{CH}_{3} \mathrm{COOH}_{(a q)}+\mathbf{N H}_{3(a q)} \rightleftharpoons \mathbf{C H}_{3} \mathbf{C O O}^{-}{ }_{(a q)}+\mathbf{N H}_{4}{ }_{(a q)}$
(Stronger Acid)
(Weaker Acid)
$K_{a}=1.8 \times 10^{-5}$
$\overline{K_{a}}=5.6 \times 10^{-10}$
b. Sodium Hydrogen Oxalate reacts with Calcium Sulfite

$$
\begin{aligned}
& \text { SA A } \\
& \text { Chemical Species Present: } \mathrm{Na}^{+}, \mathrm{HOOCCOO}{ }^{-}, \mathrm{Ca}^{2+}, \mathbf{S O}_{3}{ }^{\mathbf{2 -}}, \mathrm{H}_{2} \mathrm{O} \\
& \mathrm{~B} \quad \mathrm{SB} \quad \mathrm{~B} \\
& \text { Net-Ionic Equation: } \quad \mathrm{HOOCCOO}^{-}{ }_{(a q)}+\mathbf{S O}_{3}{ }^{2-}{ }_{(a q)} \rightleftharpoons \mathbf{O O C C O O}^{2-}{ }_{(a q)}+\mathrm{HSO}_{3}{ }_{(a q)} \\
& \text { (Stronger Acid) } \\
& K_{a}=1.5 \times 10^{-4} \\
& \text { (Weaker Acid) } \\
& K_{a}=6.3 \times 10^{-8}
\end{aligned}
$$

c. Sodium Hydrogen Carbonate reacts with Potassium Hydrogen Sulfite


Example 6: Four different weak acids are reacted with various conjugate bases, and the results are recorded as follow.

$$
\begin{aligned}
& \mathrm{HW}_{(a q)}+\mathrm{X}_{(a q)}^{-} \rightleftharpoons \mathrm{HX}_{(a q)}+\mathrm{W}_{(a q)}^{-} \quad \text { [products favoured] } \\
& \mathrm{HY}_{(a q)}+\mathrm{W}_{(a q)}^{-} \rightleftharpoons \mathrm{HW}_{(a q)}+\mathrm{Y}_{(a q)}^{-} \quad \text { [products favoured] } \\
& \mathrm{HZ}_{(a q)}+\mathrm{Y}_{(a q)}^{-} \rightleftharpoons \mathrm{HY}_{(a q)}+\mathrm{Z}_{(a q)}^{-} \quad \text { [reactants favoured] } \\
& \mathrm{HZ}_{(a q)}+\mathrm{X}_{(a q)}^{-} \rightleftharpoons \mathrm{HX}_{(a q)}+\mathrm{Z}_{(a q)}^{-} \quad \text { [reactants favoured] }
\end{aligned}
$$

List the acids in order of increasing strength.
First, we have to decide which acid is the weaker acid for each of these reactions.


Putting the inequalities together, we obtain in order of increasing acid strengths:


Assignment
17.3 pg. 604 \#17 to 20a

## 17.4: Acid-Base Indicators

Acid-Base Indicators: - chemicals that change colours at a specific pH range.

- they are themselves organic acids. Since they are usually very big structurally, we usually use abbreviations to describe them in chemical equations.
- this is due to the acidic form of the indictor (HIn) has a different colour than its basic form $\left(\mathrm{In}^{-}\right)$.

Example: Phenolphthalein $\left(\mathrm{HPh}_{(a q)} / \mathrm{Ph}_{(a q)}^{-}\right)$changes colours from colourless to pink at a pH range of 8.0 to 10.0. At its mid-range ( 9.0 - average of 8.0 and 10.0 ), the colour would be light pink (colourless + pink).
$\mathbf{H P h}_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{(I)} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}_{(a q)}^{+}+\mathrm{Ph}^{-}{ }_{(a q)} \quad K_{a}=1.0 \times 10^{-9} \quad \mathrm{p} K_{a}=9 \quad$ Colour Change $=9 \pm 1$ (Colourless) (Pink) At $\mathrm{pH} \leq 9$, phenolphthalein is colourless. At $\mathrm{pH} \geq 10$, phenolphthalein is pink.
Example: Bromothymol Blue $\left(\mathrm{HBb}_{(a q)} / \mathrm{Bb}^{-}{ }_{(a q)}\right)$ changes colours from yellow to blue at a pH range of 6.0 to 8.0. At its mid-range ( 7.0 - average of 6.0 and 8.0 ), the colour would be green (yellow + blue).
$\underset{\text { (Yellow) }}{\mathbf{H B b}_{(a q)}}+\mathrm{H}_{2} \mathrm{O}_{(l)} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}_{(a q)}^{+}+\underset{\text { (Blue) }}{\mathbf{B b}^{-}{ }_{(a q)}} \quad K_{a}=1.0 \times 10^{-7} \quad \mathrm{p} K_{a}=7 \quad$ Colour Change $=7 \pm 1$


Example 1: A sample of rainwater is poured into five test tubes. A different indicator is added to each test tube. Four of the observations are recorded in the table below.

| methyl red | yellow |
| :--- | :--- |
| phenol red | yellow |
| bromocresol green | blue |
| phenolphthalein | colourless |
| bromothymol blue | $?$ |

Determine the pH of the rainwater and the predicted colour of the sample containing bromothymol blue.
First, we need to decide on the pH range that these indicators will change colors.

| Indicators | Colour Change | $\mathbf{p H}$ range | Colour Observed | Indicated pH |
| :---: | :---: | :---: | :---: | :---: |
| methyl red | red to yellow | 4.8 to 6.0 | Yellow | $\mathrm{pH}>6.0$ |
| phenol red | yellow to red | 6.6 to 8.0 | Yellow | $\mathrm{pH}<6.6$ |
| bromocresol green | yellow to blue | 3.8 to 5.4 | Blue | $\mathrm{pH}>5.4$ |
| phenolphthalein | colourless to pink | 8.2 to 10.0 | colourless | $\mathrm{pH}<8.2$ |

From the indicated pH ranges, we can tell than the pH of the rain water is between 6.0 to 6.6. At such pH range, bromothymol blue would appear green. (The pH and colour range for bromothymol blue is $6.0-7.6$; yellow to blue)

## Assignment

Page 230.
17.4 pg. 604 \#21 to 24

## Extra Section: Environmental Issues Involving Acids and Bases

Acid Rain: - precipitation of water (rain) or (snow) that has a low pH (less than 5.0).

- natural rain is slightly acidic due to the small amount of $\mathrm{CO}_{2}$ in the atmosphere.

$$
\left.\mathrm{CO}_{2(g)}+\mathrm{H}_{2} \mathrm{O}_{(l)} \rightarrow \mathrm{H}_{2} \mathrm{CO}_{3(a q)} \quad \text { (Carbonic Acid }-K_{a}=4.5 \times 10^{-7}\right)
$$

- however, the burning of fossil fuel by vehicles and industrial activities, and also emits other oxides such as $\mathrm{NO}_{2(\mathrm{~g})}, \mathrm{SO}_{2(\mathrm{~g})}$ and $\mathrm{SO}_{3(a q)}$. These gaseous oxides (Lewis acids) combined with water in the atmosphere (Lewis base) to form various strong and weak acids. Thus, lowering the pH of rain and snow.

$$
\begin{aligned}
& \mathrm{SO}_{2(\mathrm{~g})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \rightarrow \mathrm{H}_{2} \mathrm{SO}_{3(a q)} \quad \text { (Sulfurous Acid }-K_{a}=\mathbf{1 . 4} \times \mathbf{1 0}^{\mathbf{- 2}} \text { ) } \\
& \mathrm{SO}_{3(\mathrm{~g})}+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightarrow \mathrm{H}_{2} \mathrm{SO}_{4(a q)} \\
& 2 \mathrm{NO}_{2(g)}+\mathrm{H}_{2} \mathrm{O}_{(l)} \rightarrow \mathrm{HNO}_{3(a q)}+\mathrm{HNO}_{2(a q)} \\
& \text { (Nitric Acid }-\underline{\text { Strong Acid }} \text { and Nitrous Acid }-K_{a}=4.5 \times \mathbf{1 0}^{\mathbf{- 7}} \text { ) }
\end{aligned}
$$

# Hydrogen ion concentration as pH from measurements made at the field laboratories, 1999 



National Atmospheric Deposition Program/National Trends Network http://nadp.sws.uiuc.edu
(Above) Measurements of pH in the continental U.S in 1999. Note the most severely affected regions are concentrated in the East Coast as well as in the major cities.

(Above) The Formation of Acid Rain. (Right) Measurements of pH in Eastern Canada and U.S in 1996. The lowest pHs are in the Great Lakes Region where most of the heavy industries are located.


## Effects of Acid Rain:

1. Marine Life (especially in-land lakes and rivers) is affected greatly. Acid Rain lowers the pH that can destroy all life (plants and animals). Usually, acid lake and river appears to be crystal clear, with no sign of algae, plant and animal life.
2. Vegetation (including forests) can be decimated. Since the soil acidity level are lowered, further plant growth may not be possible and the surrounding ecosystem is destroyed as a result. Forests affected by acid rain appear to be charred with trees having no leaves and all branches are brittle.

(Left) an Acid Lake. Note the clear water with the absence of life. (Right) an Acid Forest. Note the lack of leaves, the brittle branches, and the charred looked of the tree trunks.
3. In areas of where there is a sustain amount of humidity, acid rain can turn into $\underline{\text { Acid }} \mathbf{F o g}$ or $\mathbf{S m o g}_{\left(\mathbf{S O}_{2}\right.}$ $+\mathbf{H}_{2} \underline{\mathbf{O}) \text { - Combination of Smoke from Coal Burning and Fog. Humans may experience severe }}$ respiratory problems as a result. The most notable case was in London, England and surrounding areas in December 1952 when smog was so serious that there were estimated 4700 deaths.
4. Acid deposition (acid rain depositing onto a solid - metal or base that causes corrosion and neutralization) on city structures such as historical statues (usually made of limestone, $\mathrm{CaCO}_{3}$ ) and buildings can cause expensive repairs and lost of priceless arts.

(Above) Smog in London during December, 1952. (Below) Smog over the Los Angeles skyline. (Right) Acid Depositions on Statues at the Schloss Sanssouci Palace in Berlin, Germany. Note the
 black "burn" deposits on the statutes.


## Ways to Reduce Acid Rain:

1. Burn Less Fossil Fuel: drive more fuel efficient vehicles, develop alternate ways to generate electricity without combustion of fossil fuel, and reduce the amount of electricity used are all possible ways to cut down on gaseous oxides emissions.
2. Enact Legislation to Regulate Emissions: governments can pass legislation on industry to regulate the amount of gases that cause acid rain. Better filtering technology and frequent inspections of industrial facilities can hold companies accountable to these environmental laws.
3. Adding Limestone to acid lakes and rivers can raise the pH and reintroduce marine life that has been affected by acid rain.
