## Conjugate Salts

1. A salt is made up of a cation and an anion. The cation is typically a conjugate acid and the anion is typically a conjugate base. The strength of these conjugates depends on the strength of the substance from which it was derived.

2. This being the case, there are three types of salt solutions that can be formed
a. Neutral
b. Acidic
c. Basic
3. How do you determine which solution you have?
a. Neutral - no effect on the pH.

If the salt is made up of the conjugates of strong acids/bases then the salt is neutral. Remember that these conjugate have acid/base strength weaker than water - so in an aqueous solution they don't react.

For Example:

$\mathrm{Na}^{+}$, like all Group 1A and Group 2A elements are neutral in solution.
$\mathrm{NO}_{3}{ }^{-}$is the conjugate of a strong acid - meaning it is neutral in solution. In fact all of the conjugates of strong acids are neutral in solution. It is a relatively short list to remember. Along with $\mathrm{NO}_{3}{ }^{-}$, the list also includes $\mathrm{Cl}^{-}, \mathrm{ClO}_{4}{ }^{-}, \mathrm{Br}^{-}, \mathrm{I}^{-}$, and $\mathrm{ClO}_{3}^{-}$. The conjugates of $\mathrm{H}_{2} \mathrm{SO}_{4}$ are not included because things get more complicated with polyprotic acids.

## b. Acidic - lowers pH

If the salt is made up of a cation that is the conjugate of a weak base and an anion that is the conjugate of a strong acid then the salt is acidic. Remember that the conjugate of a weak base is an acid stronger than water.

For Example:

$\mathrm{NH}_{4}{ }^{+}$is the conjugate of the weak acid, $\mathrm{NH}_{3}$. This means that if this salt was put in solution, the following reaction would take place:

$$
\mathrm{NH}_{4(\mathrm{aq})}^{+}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{p})} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}{ }_{(\mathrm{aq})}+\mathrm{NH}_{3(\mathrm{aq})}
$$

$\mathrm{Cl}^{-}$is neutral in solution, as it is the conjugate of a strong acid. So it has no effect on the pH of the solution.
c. Basic - raises pH

> If the salt is made up of an anion that is the conjugate of a weak acid and a cation that is the conjugate of a strong base the salt is basic. Remember that the conjugate of a weak acid is a base stronger than water.

For Example:

$\mathrm{CH}_{3} \mathrm{COO}^{-}$is the conjugate base of a weak acid. This means that if this salt was placed in solution, the following reaction would take place:

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

$\mathrm{Na}^{+}$is a group 1 cation, so it has no effect on the pH of the solution.

## 4. How do conjugate pairs equilibrium values relate?

Remember a conjugate pair differ by only one $\mathrm{H}^{+}$. The acid has one more $\mathrm{H}^{+}$than the base.

$$
K_{a} x K_{b}=K_{w}
$$

This means that, for a conjugate pair, if you know the equilibrium constant for one, you can solve for the other.
5. What if both conjugates have strength?

You would then need to compare the $K_{a}$ value of the cation with the $K_{b}$ value of the anion.

If:

$$
\begin{aligned}
& K_{a}=K_{b} \text { the solution is neutral } \\
& K_{a}>K_{b} \text { the solution is acidic } \\
& K_{a}<K_{b} \text { the solution is basic. }
\end{aligned}
$$

For Example:


$$
K a>K_{b} \text { the solution is acidic }
$$

6. Calculate the pH of a $0.12 \mathrm{M} \mathrm{KNO}_{2}$ solution. $\left(\mathrm{K}_{\mathrm{a}}=4.0 \times 10^{-4}\right)$.

The first thing you want to do is determine the type of salt that you have


This is a basic salt
$\mathrm{NO}_{2}{ }^{-}$will react in aqueous solution.

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

$$
K_{b}=\frac{[-\mathrm{OH}]\left[\mathrm{HNO}_{2}\right]}{\left[\mathrm{NO}_{2}^{-}\right]}
$$

This problem is asking for pH which means, that I need to solve for the concentration of $\mathrm{H}^{+}$at equilibrium. If you notice there is no $\mathrm{H}^{+}$formed directly by this reaction. That does not mean that there isn't any $\mathrm{H}^{+}$in the solution though. This salt is placed in water. Water undergoes autoionization - meaning it produces $\mathrm{H}^{+}$. The amount of $\mathrm{H}^{+}$it produces is affected by the addition of the basic salt. Remember that

$$
\left[\mathrm{H}^{+}\right][\mathrm{OH}]=K_{w}=1.0 \times 10^{-14}
$$

So if you determine the concentration of $\left[\mathrm{OH}^{-}\right]$you can solve for the concentration of $\left[\mathrm{H}^{+}\right]$.

Alternatively, you could solve for the pOH and use the relationship

$$
p H+p O H=14
$$

Both methods start with the ICE chart:

| $\mathrm{NO}_{2}{ }^{-}(\mathrm{aq})+$ |  | $\mathrm{H}_{2} \mathrm{O}$ | $\rightleftharpoons \mathrm{HNO}$ | ${ }^{-} \mathrm{OH}{ }_{(a q)}$ |
| :---: | :---: | :---: | :---: | :---: |
| I | 0.12 M | - | 0 | 0 |
| C | $-x$ | - | $+x$ | $+x$ |
| E | $0.12-x$ | - | $x$ | $x$ |

$$
K_{b}=\frac{(x)(x)}{(0.12-x)}
$$

You have $K_{a}$ not $K_{b}$. This means you need to solve for $K_{b}$ using

$$
\begin{gathered}
K_{a} \times K_{b}=K_{w} \\
K_{b}=\frac{K_{w}}{K_{a}}=\frac{1.0 \times 10^{-14}}{4.0 \times 10^{-4}}=2.5 \times 10^{-11}
\end{gathered}
$$

Now that you have $K_{b}$, you can plug it into the equation.

$$
K_{b}=\frac{x^{2}}{(0.12-x)}=2.5 \times 10^{-11}
$$

Because $K_{b} \ll 1$ you can make the assumption that $0.12-x=0.12$

$$
\begin{gathered}
\frac{x^{2}}{0.12}=2.5 \times 10^{-11} \\
x=1.73 \times 10^{-6} \\
\frac{1.73 \times 10^{-6}}{0.12} \times 100=1.44 \times 10^{-5} \%
\end{gathered}
$$

more than meets the $5 \%$ rule.

Now you know the equilibrium concentration of ${ }^{-} \mathrm{OH}$. At this point you can either solve for the $\left[\mathrm{H}^{+}\right]$or solve for the pOH . I'm going to solve for the pOH .

$$
\begin{gathered}
p O H=-\log [O H]=-\log \left(1.73 \times 10^{-6}\right)=5.76 \\
p H=14-p O H=14-5.76=8.24
\end{gathered}
$$

7. Arrange the following in order of acidic to most basic $\mathrm{CaBr}_{2}, \mathrm{KNO}_{2}, \mathrm{HClO}_{4}, \mathrm{HNO}_{2}, \mathrm{HONH}_{3} \mathrm{ClO}_{4}$

Your first step is to identify what type of substance each compound is meaning a salt, acid or base. If it is a salt break it up into its component pieces and determine their relative acid/base strengths of each.

strong acid $\mathrm{HClO}_{4}$
weak acid $\mathrm{HNO}_{2}$ $K_{0}=4.0 \times 10^{-6}$

salt
$\mathrm{HONH}_{3} \mathrm{ClO}_{4}$


Now we need to order these substances from most acidic to least acidic. Strongest acidic $\rightarrow$ Strongest base

$$
\mathrm{HClO}_{4}>\mathrm{HNO}_{2} \text { (higher } \mathrm{K}_{\mathrm{a}} \text { value) }>\mathrm{HONH}_{3} \mathrm{ClO}_{4}>\mathrm{CaBr}_{2}>\mathrm{KNO}_{2}
$$

8. $\mathrm{NaN}_{3}$ is added to water. Calculate the pH of a 0.010 M sol'n. ( $К а=1.9 \times 10^{-5}$ )

Before you can determine what the reaction equation is - you have to figure out if you have an acidic or basic salt.

basic salt

$$
\begin{gathered}
\mathrm{N}_{3}^{-}{ }_{(a q)}+\mathrm{H}_{2} \mathrm{O}_{(l)} \rightleftharpoons \mathrm{HN}_{3}(\mathrm{aq})+{ }^{-} \mathrm{OH}(a q) \\
K_{b}=\frac{\left[H N_{3}\right]\left[^{-} \mathrm{OH}\right]}{\left[\mathrm{N}_{3}-\right]}
\end{gathered}
$$

Make the ICE chart...

| $\mathrm{N}_{3}{ }^{-}(\mathrm{aq})$ |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| + | $\mathrm{H}_{2} \mathrm{O}_{(l)}$ | $\stackrel{y y}{c \mid} \mathrm{HN}_{{ }_{(a q)}}+$ | ${ }_{\text {(aq) }}$ |  |
| $I$ | $0.010 M$ | - | 0 | 0 |
| $C$ | $-x$ | - | $+x$ | $+x$ |
| $E$ | $0.010-x$ | - | $x$ | $x$ |

Once again we plug into the equilibrium expression to determine x .
Remember that you will be plugging into the expression for $K_{b}$ - because this is a base reaction. In the problem they gave you the $K_{a}$ for the conjugate acid $\mathrm{HN}_{3}$ - so you will first need to solve for $\mathrm{K}_{\mathrm{b}}$.

$$
K_{b}=\frac{K_{w}}{K_{a}}=\frac{1 \times 10^{-14}}{1.9 \times 10^{-5}}=5.26 \times 10^{-10}
$$

Now you can plug in and solve for x .

$$
5.26 \times 10^{-10}=\frac{x^{2}}{0.010-x}
$$

As $K_{b}$ is quite a small number, you are safe to assume that the change to the starting concentration is negligible.

$$
\begin{gathered}
5.26 \times 10^{-10}=\frac{x^{2}}{0.010} \\
x=2.30 \times 10^{-6}
\end{gathered}
$$

Using the 5\% rule make sure your assumption was valid

$$
\frac{2.30 \times 10^{-6}}{0.010} \times 100=0.02 \%
$$

This answer is well within the parameters of being valid.
Once again the $x$ value that you have calculated for relates to the [ ${ }^{-} \mathrm{OH}$ ]. So you will initially solve for pOH and then use that value to determine pH .

$$
\begin{gathered}
p O H=-\log [-O H]=-\log \left(2.30 \times 10^{-6}\right)=5.63 \\
p H=14-p O H=14-5.63=8.37
\end{gathered}
$$

