## AP CHEMISTRY

Topic 7: Acids \& BASES, PART D
Day 81:

- Polyprotic acids
- Amphoteric substance
- Acid-Base salts

1. Write out the stepwise dissociation reactions and the $K_{a}$ expressions for the diprotic acid $\mathrm{H}_{2} \mathrm{SO}_{3}$.

$$
\begin{aligned}
& \mathrm{H}_{2} \mathrm{SO}_{3} \leftrightarrow \mathrm{HSO}_{3}^{-1}+\mathrm{H}^{+1} \frac{\left[\mathrm{HSO}_{3}^{-1}\right]\left[\mathrm{H}^{+1}\right]}{\left[\mathrm{H}_{2} \mathrm{SO}_{3}\right]} \\
& \mathrm{HSO}_{3}^{-1} \leftrightarrow \mathrm{SO}_{3}^{-2}+\mathrm{H}^{+1} \frac{\left[\mathrm{SO}_{3}^{-2}\right]\left[\mathrm{H}^{+1}\right]}{\left[\mathrm{HSO}_{3}^{-1}\right]}
\end{aligned}
$$

2. Calculate the pH of a $0.10 \mathrm{M} \mathrm{H}_{2} \mathrm{CO}_{3}\left(K_{a_{1}}=4.3 \times 10^{-7}, K_{a_{2}}=4.3 \times 10^{-11}\right)$.

|  | $\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]$ | + | $\left[\mathrm{H}_{2} \mathrm{O}\right]$ | $\leftrightarrow$ | $\left[\mathrm{HCO}_{3}^{-1}\right]$ | + | $\left[\mathrm{H}_{3} \mathrm{O}^{+1}\right]$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{I}$ | $0.10 M$ |  | - |  | 0 |  | 0 |
| $\mathbf{C}$ | $-x$ |  | - |  | $+x$ |  | $+x$ |
| $\mathbf{E}$ | $0.10 M-x$ |  | - |  | $x$ |  | $x$ |

$$
\begin{gathered}
K_{a_{1}}=4.3 \times 10^{-7}=\frac{\left[\mathrm{HCO}_{3}^{-1}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+1}\right]}{\left[\mathrm{H}_{2} \mathrm{CO}_{3}\right]}=\frac{x^{2}}{0.10-x}=\frac{x^{2}}{0.10} \\
x^{2}=(0.10)\left(4.3 \times 10^{-7}\right), \quad x=\sqrt{4.3 \times 10^{-8}}=2.07 \times 10^{-4} \\
{\left[\mathrm{H}_{3} \mathrm{O}^{+1}\right]=2.1 \times 10^{-4} M} \\
\mathbf{p H}=-\log \left(2.1 \times 10^{-4}\right)=\mathbf{3 . 6 8}
\end{gathered}
$$

There is no need to do a second ICE chart since the $\mathbf{p H}$ will not change by significant amount... If you do a second ICE chart, the concentration of the $\left[\mathrm{H}^{+1}\right]=4.30 \times 10^{-11} M$. This concentration is so small it will NOT affect the $\mathbf{p H}$.
3. Given that the $K_{a}$ value for acetic acid is $1.8 \times 10^{-5}$ and the $K_{a}$ value for hypochlorous acid is $3.5 \times 10^{-8}$, which is the stronger base, $\mathrm{OCl}^{-1}$ or $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-1}$ ? Explain why.

From the $K_{a}$ values, acetic acid is a stronger acid than hypochlorous acid. Conversely, the conjugate base of acetic acid, $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-1}$, will be a weaker base than the conjugate base of hypochlorous acid, $\mathrm{OCl}^{-1}$, Thus, the hypochlorite ion, $\mathrm{OCl}^{-1}$, is a stronger base than the acetate ion, $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}{ }^{-1}$, In general, the stronger acid, the weaker the conjugate base. This statement comes from the relationship $K_{w}=K_{a} \times K_{b}$ which holds true for all conjugate acid-base pairs.

Also, you could calculate the $K_{b}$ for each the of bases... A higher $K_{b}$ equals the stronger base...
$\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-1}: \quad K_{b}=\frac{K_{w}}{K_{a}}=\frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}}=5.56 \times 10^{-10} \quad ; \quad \mathrm{OCl}^{-1} \quad: \quad K_{b}=\frac{K_{w}}{K_{a}}=\frac{1.00 \times 10^{-14}}{3.5 \times 10^{-8}}=2.86 \times 10^{-7}$
4. Calculate the pH for $0.10 \mathrm{MCH}_{3} \mathrm{NH}_{3} \mathrm{Cl}, K_{b}=4.38 \times 10^{-4}$ for $\mathrm{CH}_{3} \mathrm{NH}_{2}$.

$$
\mathrm{CH}_{3} \mathrm{NH}_{3} \mathrm{Cl} \rightarrow \mathrm{CH}_{3} \mathrm{NH}_{3}^{+1}+\mathrm{Cl}^{-1}
$$

$\left(\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+1}\right.$, conjugate acid of a weak base, $\mathrm{Cl}^{-1}$, conjugate base of a strong acid )
The chlorine ion, $\mathrm{Cl}^{-1}$, has no effect on the solution to make it basic or acidic.

$$
K_{a}=\frac{K_{w}}{K_{b}}=\frac{1.00 \times 10^{-14}}{4.38 \times 10^{-4}}=2.28 \times 10^{-11}
$$

|  | $\left[\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+1}\right]$ | + | $\left[\mathrm{H}_{2} \mathrm{O}\right]$ | $\rightleftharpoons$ | $\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right]$ | + | $\left[\mathrm{H}_{3} \mathrm{O}^{+1}\right]$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{I}$ | 0.10 M |  | - |  | 0 |  | 0 |
| $\mathbf{C}$ | $-x$ |  | - |  | $+x$ |  | $+x$ |
| $\mathbf{E}$ | $0.10 \mathrm{M}-x$ |  | - |  | $x$ |  | $x$ |

$$
\begin{gathered}
K_{a}=2.28 \times 10^{-11}=\frac{\left[\mathrm{CH}_{3} \mathrm{NH}_{2}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+1}\right]}{\left[\mathrm{CH}_{3} \mathrm{NH}_{3}^{+1}\right]}=\frac{x^{2}}{0.10-x}=\frac{x^{2}}{0.10} \\
x^{2}=(0.10)\left(2.28 \times 10^{-11}\right), \quad x=\sqrt{2.28 \times 10^{-12}}=1.51 \times 10^{-6} \\
{\left[\mathrm{H}_{3} \mathrm{O}^{+1}\right]=1.51 \times 10^{-6} \mathrm{M}} \\
\mathbf{p H}=-\log \left(1.51 \times 10^{-6}\right)=\mathbf{5 . 8 2}
\end{gathered}
$$

5. Calculate the pH for $0.050 \mathrm{M} \mathrm{NaCN}, K_{a}=6.2 \times 10^{-10}$ for HCN .

$$
\mathrm{NaCN} \rightarrow \mathrm{Na}^{+1}+\mathrm{CN}^{-1}
$$

( $\mathrm{Na}^{+1}$, conjugate acid of a strong base, $\mathrm{CN}^{-1}$, conjugate base of a weak acid )
The sodium ion, $\mathrm{Na}^{+1}$, has no effect on the solution to make it basic or acidic.

$$
K_{b}=\frac{K_{w}}{K_{a}}=\frac{1.00 \times 10^{-14}}{6.2 \times 10^{-10}}=1.61 \times 10^{-5}
$$

|  | $\left[\mathrm{CN}^{-1}\right]$ | + | $\left[\mathrm{H}_{2} \mathrm{O}\right]$ | $\rightleftharpoons$ | $[\mathrm{HCN}]$ | + | $\left[\mathrm{OH}^{-1}\right]$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{I}$ | 0.050 M |  | - |  | 0 |  | 0 |
| $\mathbf{C}$ | $-x$ |  | - |  | $+x$ |  | $+x$ |
| $\mathbf{E}$ | $0.050 M-x$ |  | - |  | $x$ |  | $x$ |

$$
\begin{gathered}
K_{b}=1.61 \times 10^{-5}=\frac{[H C N]\left[O H^{-1}\right]}{\left[C N^{-1}\right]}=\frac{x^{2}}{0.050-x}=\frac{x^{2}}{0.050} \\
x^{2}=(0.050)\left(1.61 \times 10^{-5}\right), \quad x=\sqrt{8.06 \times 10^{-7}}=8.98 \times 10^{-4} \\
{\left[\mathrm{OH}^{-1}\right]=8.98 \times 10^{-4} \mathrm{M}} \\
\mathrm{pOH}=-\log \left(8.98 \times 10^{-4}\right)=3.05 \\
\mathbf{p H}=14-3.05=\mathbf{1 0 . 9 5}
\end{gathered}
$$

6. An unknown salt is either $\mathrm{NaCN}, \mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}, \mathrm{NaF}, \mathrm{NaCl}, \mathrm{NaNO}_{2}$, or NaOCl . When 0.100 mol of the salt is dissolved in 1.00 liter of water, the pH of the solution is 8.07 . What is the identity of this salt? (use the chart below)

|  |  |  |
| :--- | :--- | :--- |
| Values of $K_{\mathrm{a}}$ for Some Common Monoprotic Acids |  |  |
| Normula | Name | Value of $K_{\mathrm{a}}{ }^{\star}$ |
| $\mathrm{HSO}_{4}^{-}$ | Hydrogen sulfate ion | $1.2 \times 10^{-2}$ |
| $\mathrm{HClO}_{2}$ | Chlorous acid | $1.2 \times 10^{-2}$ |
| $\mathrm{HC}_{2} \mathrm{H}_{2} \mathrm{ClO}_{2}$ | Monochloracetic acid | $1.35 \times 10^{-3}$ |
| $\mathrm{HF}^{\mathrm{HNO}_{2}}$ | Hydrofluoric acid | $7.2 \times 10^{-4}$ |
| $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ | Nitrous acid | $4.0 \times 10^{-4}$ |
| $\left[{\left.\mathrm{Al}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}}^{\mathrm{HOCl}^{-4}}\right.$ | Acetic acid | $1.8 \times 10^{-5}$ |
| $\mathrm{HCN}^{2}$ | Hydrated aluminum(III) ion | $1.4 \times 10^{-5}$ |
| $\mathrm{NH}_{4}^{+}$ | Hypochlorous acid | $3.5 \times 10^{-8}$ |
| $\mathrm{HOC}_{6} \mathrm{H}_{5}$ | Hydrocyanic acid | $6.2 \times 10^{-10}$ |
|  | Ammonium ion | $5.6 \times 10^{-10}$ |

## Answers:

All these salts contain $\mathrm{Na}^{+1}$ which has no acidic / basic properties and a conjugate base of a weak acid ( except for NaCl where $\mathrm{Cl}^{-1}$ is a neutral species. ) All conjugates bases of weak acids are weak bases since $K_{b}$ for these species are between $K_{w}$ and one (1). To identify the species, we will use the data given (in the chart above ) to determine the $K_{b}$ value for the weak conjugate base. From the $K_{b}$ value and the data above, we can identify the conjugate base present by calculating $K_{a}$ value for the weak acid.

|  | $\left[\mathrm{A}^{-1}\right]$ | + | $\left[\mathrm{H}_{2} \mathrm{O}\right]$ | $\rightleftharpoons$ | $[\mathrm{HA}]$ | + | $\left[\mathrm{OH}^{-1}\right]$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{I}$ | $0.100 M$ |  | - |  | 0 |  | 0 |
| $\mathbf{C}$ | $-x$ |  | - |  | $+x$ |  | $+x$ |
| $\mathbf{E}$ | $0.100 M-x$ |  | - |  | $x$ |  | $x$ |

$$
\begin{gathered}
K_{b}=\frac{[H A]\left[O H^{-1}\right]}{\left[A^{-1}\right]}=\frac{x^{2}}{(0.100-x)} \\
\mathrm{pH}=8.07(\text { given from question ) } \\
\mathrm{pOH}=14.00-8.07=5.93 \\
{\left[\mathrm{OH}^{-1}\right]=x=\text { antilog }(-5.93)=1.17 \times 10^{-6} \mathrm{M}} \\
K_{b}=\frac{\left(1.17 \times 10^{-6}\right)^{2}}{\left(0.100-1.17 \times 10^{-6}\right)}=1.38 \times 10^{-11}=\text { For "Unknown Salt" }
\end{gathered}
$$

Since we are NOT given $K_{b}$ values for the Salts, we must find the $K_{a}$ for the conjugate acid.

$$
K_{a}=\frac{K_{w}}{K_{b}}=\frac{1.00 \times 10^{-14}}{1.38 \times 10^{-11}}=7.24 \times 10^{-4}
$$

from the table above, this $K_{a}$ value is closest to HF, Therefore the unknown salt is NaF.

