## Weak Acid Calculation - When the Assumption Fails

Since the acid dissociates less than $5 \%, \Delta$ is negligible. A good rule of thumb, if the value of the equilibrium constant is about $1 \times 10^{-5}$ or less and the $W A$ or $W B$ concentration $\geq 0.01 \mathrm{M}$, the assumption is valid.

Calculate the equilibrium concentrations of $\mathrm{H}_{3} \mathrm{O}^{+}, \mathrm{HClO}_{2}$, and $\mathrm{ClO}_{2}{ }^{-}$for a $0.10 \mathrm{M} \mathrm{HClO}_{2}$ solution $\left(K_{a}=1.1 \times 10^{-2}\right)$

1. Set up the reaction:

$$
\mathrm{HClO}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{ClO}_{2}^{-}
$$

2. Set up the chart:

> Initial:

$$
\begin{array}{ccc}
{\left[\mathbf{H C l O}_{\mathbf{2}}\right]} & {\left[\mathbf{H}_{3} \mathbf{O}^{+}\right]} & {\left[\mathrm{ClO}_{\mathbf{2}}^{-}\right]} \\
0.10 \mathrm{M} & 0 & 0
\end{array}
$$

Equilibrium: $\quad 0.10 \mathrm{M}-\Delta$
$\Delta=\mathbf{x}$
3. Write the $K_{a}$ expression:

$$
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{ClO}_{2}^{-}\right]}{\left[\mathrm{HClO}_{2}\right]}
$$

4. Substitute:

$$
1.1 \times 10^{-2}=\frac{(\Delta)(\Delta)}{(0.10-\Delta)}=\frac{\Delta^{2}}{(0.10-\Delta)}
$$

5. Assume that ${ }_{\Delta}$ is negligible when subtracted.

$$
\frac{\Delta^{2}}{(0.10-\Delta)} \rightarrow \frac{\Delta^{2}}{(0.10)}
$$

6. Solve for $\Delta$ -

$$
\begin{aligned}
\frac{\Delta^{2}}{(0.10)} & =1.1 \times 10^{-2} \\
\Delta^{2} & =(0.10)\left(1.1 \times 10^{-2}\right) \\
\Delta & =\sqrt{(0.10)\left(1.1 \times 10^{-2}\right)} \\
\Delta & =0.033 \mathrm{M}
\end{aligned}
$$

## 7. Check the assumption.

$$
\frac{\Delta}{\text { initial }} \times 100=\frac{0.033 \mathrm{M}}{0.10 \mathrm{M}} \times 100=33 \%>5 \%
$$

The assumption fails so we have to go back to the expression before the assumption:

$$
1.1 \times 10^{-2}=\frac{\Delta^{2}}{(0.10-\Delta)}
$$

We have to now solve for $\Delta$ by using the quadratic formula. In order to use the quadratic formula, our equation has to be in the standard form:

$$
a x^{2}+b x+c=0
$$

So we have to rearrange our equation to fit the standard form:

$$
\begin{aligned}
& 1.1 \times 10^{-2}=0.011=\frac{\Delta^{2}}{(0.10-\Delta)} \quad \text { Multiply both sides by }(0.10-\Delta) \\
& 0.011(0.10-\Delta)=\Delta^{2} \quad \text { Distribute } 0.011 \text { to both terms inside the parentheses } \\
& 0.0011-0.011 \Delta=\Delta^{2} \quad \text { Move all the terms on the left side of the equation } \\
& \text { to the right by adding the opposite of each term } \\
& \Delta^{2}+0.011 \Delta-0.0011=0 \\
& a=1 \quad b=0.011 \quad c=-0.0011
\end{aligned}
$$

The quadratic formula is:

$$
\mathrm{x}=\frac{-\mathrm{b} \pm \sqrt{\mathrm{b}^{2}-4 \mathrm{ac}}}{2 \mathrm{a}}
$$

Substitute in the values we found for $a, b$, and $c$ and solve for ${ }_{\Delta}$ :

$$
\begin{aligned}
& \mathrm{a}=1 \quad \mathrm{~b}=0.011 \quad \mathrm{c}=-0.0011 \\
& \Delta=\frac{-\mathrm{b} \pm \sqrt{\mathrm{b}^{2}-4 \mathrm{ac}}}{2 \mathrm{a}}=\frac{-0.011+\sqrt{(0.011)^{2}-4(1)(-0.0011)}}{2(1)}=0.028 \mathrm{M}
\end{aligned}
$$

According to our chart, $\Delta^{=}=\left[\mathbf{H}_{\mathbf{3}} \mathbf{O}^{+}\right]=\left[\mathbf{C l O}_{\mathbf{2}}{ }^{-}\right]$and $\left[\mathbf{H C l O}_{\mathbf{2}}\right]=0.10{ }^{-} \mathrm{\Delta}^{\text {: }}$

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left[\mathrm{ClO}_{2}^{-}\right]=\Delta=0.028 \mathrm{M}
$$

$$
\left[\mathrm{HClO}_{2}\right]=0.10-0.028=0.072 \mathrm{M}
$$

ex. What are the concentrations of all species present in a 0.50 M acetic acid solution? The Ka is $1.7 \times 10^{-5}$
(p.8)

POLYPROTIC ACIDS: A weak acid that supplies two or more hydronium ions per molecule. (Refer to the dissociation WS for the dissociation reactions of these.)
$\mathrm{H}_{3} \mathrm{PO}_{4} \quad \mathrm{Kal}=5.9 \times 10^{-3}$
$\mathrm{H}_{2} \mathrm{PO}_{4}^{-} \quad \mathrm{Ka} 2=6.2 \times 10-8$
$\mathrm{HPO}_{4}{ }^{2-} \quad \mathrm{Ka} 3=4.8 \times 10^{-13}$

The dissociation constants decrease with each successive step. It is easier to remove an $\mathrm{H}+$ from an uncharged species and becomes increasingly more difficult as the negative charge on the ions gets larger.
ex. Calculate the equilibrium concentrations of $\mathrm{H}_{2} \mathrm{~S}, \mathrm{H}_{3} \mathrm{O}^{+}$, HS -, and $\mathrm{S}^{-2}$ present in a 0.10 M solution of $\mathrm{H}_{2} \mathrm{~S}$.
(p.10)

$$
\begin{array}{lll}
\mathrm{H}_{2} \mathrm{~S}+\mathrm{H}_{2} \mathrm{O}---->\mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{HS}- & \mathrm{Ka} 1=1.1 \times 10^{-7} \\
\text { HS- }+\mathrm{H}_{2} \mathrm{O}---->\mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{S}^{-2} & \mathrm{Ka} 2=1.0 \times 10^{-14}
\end{array}
$$

Because $\mathrm{Ka} 1 \ggg \mathrm{Ka}$ 2, we may assume nearly all of the $\mathrm{H}_{3} \mathrm{O}^{+}$is derived from the $1^{\text {st }}$ dissociation and that very little of HS- formed in the $1^{\text {st }}$ step will undergo further dissociation.

