Weak Acid Calculation - When the Assumption Fails

Since the acid dissociates less than 5%, Δ is negligible. A good rule of thumb, if the value of the equilibrium constant is about 1 x 10⁻⁵ or less and the WA or WB concentration \geq 0.01 M, the assumption is valid.

Calculate the equilibrium concentrations of H_3O^+ , $HClO_2$, and ClO_2^- for a 0.10 M HClO₂ solution ($K_a = 1.1 \times 10^{-2}$)

1. Set up the reaction:

$$HClO_2 + H_2O \rightleftharpoons H_3O^+ + ClO_2^-$$

2. Set up the chart:

	[HClO ₂]	[H ₃ O ⁺]	[ClO ₂ ⁻]
Initial:	0.10 M	0	0
<u>Equilibrium:</u>	0.10 M - Δ	Δ	Δ

 $\Delta = \mathbf{x}$

3. Write the K_a expression:

$$K_{a} = \frac{[H_{3}O^{+}][ClO_{2}^{-}]}{[HClO_{2}]}$$

4. Substitute:

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

5. Assume that Δ is negligible when subtracted.

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

6. Solve for Δ .

$$\frac{\Delta^2}{(0.10)} = 1.1 \times 10^{-2}$$
$$\Delta^2 = (0.10)(1.1 \times 10^{-2})$$
$$\Delta = \sqrt{(0.10)(1.1 \times 10^{-2})}$$
$$\Delta = 0.033 \text{ M}$$

7. Check the assumption.

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

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

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

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

$$ax^2 + bx + c = 0$$

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

$$1.1 \times 10^{-2} = 0.011 = \frac{\Delta^2}{(0.10 - \Delta)}$$
Multiply both sides by $(0.10 - \Delta)$

$$0.011(0.10 - \Delta) = \Delta^2$$
Distribute 0.011 to both terms inside the parentheses
$$0.0011 - 0.011\Delta = \Delta^2$$
Move all the terms on the left side of the equation to the right by adding the opposite of each term
$$\Delta^2 + 0.011\Delta - 0.0011 = 0$$

The quadratic formula is:

a = 1 b = 0.011 c = -0.0011

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

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

a = 1 b = 0.011 c = -0.0011

$$\Delta = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.011 + \sqrt{(0.011)^2 - 4(1)(-0.0011)}}{2(1)} = \boxed{0.028 \text{ M}}$$

According to our chart, $\Delta = [\mathbf{H}_3\mathbf{O}^+] = [\mathbf{ClO}_2^-]$ and $[\mathbf{HClO}_2] = 0.10 - \Delta$:

$$[H_3O^+] = [ClO_2^-] = \Delta = 0.028M$$

 $[HClO_2] = 0.10-0.028 = 0.072M$

ex. What are the concentrations of all species present in a 0.50 M acetic acid solution? The Ka is 1.7×10^{-5}

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.)

H_3PO_4	$Ka1 = 5.9 \times 10^{-3}$
$H_2PO_4^-$	$Ka2 = 6.2 \times 10-8$
HPO_4^{2-}	$Ka3 = 4.8 \times 10^{-13}$

The dissociation constants decrease with each successive step. It is easier to remove an 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 H_2S , H_3O^+ , HS-, and S⁻² present in a 0.10 M solution of H_2S .

(p.10)

 $H_2S + H_2O ----> H_3O^+ + HS- Ka1 = 1.1 \times 10^{-7}$

HS- + H_2O -----> H_3O^+ + S^{-2} Ka2 = 1.0 x 10⁻¹⁴

Because Ka1>>>Ka2, we may assume nearly all of the $H_3 O^+$ is derived from the 1st dissociation and that very little of HS- formed in the 1st step will undergo further dissociation.