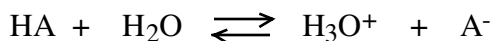


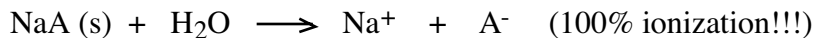
# TYPE 2 (acid buffer)

(both HA and A<sup>-</sup> put in solution)

For a weak acid (HA) in water:

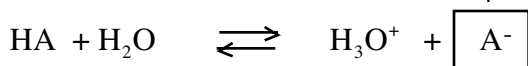
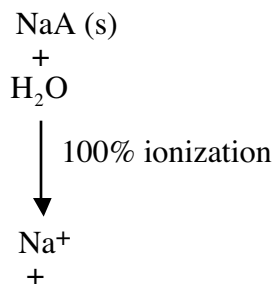


For a salt, NaA, of the weak acid (HA) in water:



**NOTICE:** There are now TWO sources for the ion A<sup>-</sup>. When there is more than one source for an ion in solution, this is called the COMMON ION EFFECT. Please be VERY aware that the main source for the ion, A<sup>-</sup>, is from the salt and not from the acid. This is the key to understanding TYPE 2 problems.

Here, the two reactions are shown intersecting at the point of the common ion.



The following equilibrium condition still applies:  $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$

now let C<sub>HA</sub> be the analytical concentration (label) of the weak acid (HA) and C<sub>A<sup>-</sup></sub> be the concentration of the salt of the weak acid (NaA, or a better term, the conjugate base concentration, [A<sup>-</sup>]).

Our Equilibrium "Chart"

|         | [HA]                | [H <sup>+</sup> ] | [A <sup>-</sup> ]              |
|---------|---------------------|-------------------|--------------------------------|
| initial | C <sub>HA</sub>     | 0                 | C <sub>A<sup>-</sup></sub>     |
| change  | -x                  | +x                | +x                             |
| final   | C <sub>HA</sub> - x | x                 | C <sub>A<sup>-</sup></sub> + x |

$$K_a = \frac{x(C_{A^-} + x)}{(C_{HA} - x)} \quad \text{Equation 2.1}$$

$$K_a C_{HA} - K_a(x) = C_{A^-}(x) + x^2$$

$$0 = x^2 + (K_a + C_{A^-})(x) - K_a C_{HA}$$

$$[\text{H}^+] = x = \frac{-(K_a + C_{\text{A}^-}) + \sqrt{(K_a + C_{\text{A}^-})^2 + 4K_a C_{\text{HA}}}}{2}$$

This equation is the exact solution for calculating the  $[\text{H}^+]$  for any solution made by mixing both a concentration of weak acid AND a concentration of the salt of the weak acid in water.

**NOTE: you should** (almost) **never ever have to use this equation. Why? continue...**

If  $K_a$  is small enough (less than  $10^{-4}$ ) and there are REASONABLE concentrations for HA and  $\text{A}^-$ , the following assumption can and should be made:

$$\begin{aligned} C_{\text{HA}} - x &\cong C_{\text{HA}} && \text{all this is saying is that } x \text{ is so small compared to } C_{\text{HA}}, \text{ it doesn't change it} \\ C_{\text{A}^-} + x &\cong C_{\text{A}^-} && \text{this is saying the same thing except compared to } C_{\text{A}^-}, \text{ it doesn't change it} \end{aligned}$$

So that Equation 2.1 shown above becomes

$$K_a = \frac{x(C_{\text{A}^-})}{(C_{\text{HA}})}$$

and solving:

$$[\text{H}^+] = x = K_a \left( \frac{C_{\text{HA}}}{C_{\text{A}^-}} \right) \quad \text{Equation 2.2}$$

This equation is the approximate solution for calculating the  $[\text{H}^+]$  for any solution made by mixing both a concentration of weak acid (HA) AND a concentration of the salt of that weak acid (NaA) in water. As long as any REASONABLE concentration of HA and NaA are used, this "approximation" is really almost EXACT!! Notice that it is Equation 2.2 shown above that is the basis for the Henderson-Hasselbalch Equation. The *-log* function is taken on both sides of Equation 2.2 to give the Henderson-Hasselbalch Equation for acids:

$$\text{pH} = \text{p}K_a + \log \left( \frac{C_{\text{A}^-}}{C_{\text{HA}}} \right) \quad \text{Henderson-Hasselbalch Equation for Acids}$$

Because the  $\text{A}^-$  usually comes from a salt, sometimes the H-H Equation is written in the following form:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{SALT}]}{[\text{ACID}]} \quad \text{Henderson-Hasselbalch Equation for Acids}$$