TYPE 2 (acid buffer)

(both HA and A- are put into solution)

For a weak acid (HA) in water:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

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

$$NaA(s) + H_2O \rightleftharpoons Na^+ + A^- (100\% ionization!!!)$$

NOTICE: There are now TWO sources for the ion A⁻. 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 <u>main</u> source for the ion, A⁻, is from the <u>salt</u> and not from the acid. This is the key to understanding TYPE 2 problems.

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

now let C_{HA} be the analytical concentration (label) of the weak acid (HA) and C_{A-} be the concentration of the salt of the weak acid (NaA, or a better term, the conjugate base concentration, [A-]).

Our Equilibrium "ICE" Table

	[HA]	[H+]	[A-]
initial	$C_{ m HA}$	0	C_{A} -
change	- <i>x</i>	+x	+x
equilibrium	$C_{\rm HA} - x$	x	$C_{A^-} + x$

$$K_{a} = \frac{x(C_{A^{-}} + x)}{(C_{HA} - x)}$$
 Equation 2.1

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

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

solve with quadratic formula...

TYPE 2 (acid buffer) continued

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

This equation is the <u>exact</u> solution for calculating the [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 A-, the following assumption can and should be made:

 $C_{HA} - x \cong C_{HA}$ all this is saying is that x is so small compared to C_{HA} , it doesn't change it

 $C_{A^-} + x \cong C_{A^-}$ this is saying the same thing except compared to C_{A^-} , it doesn't change it

So that Equation 2.1 shown above becomes

$$K_{\rm a} = \frac{x \left(C_{\rm A^-} \right)}{\left(C_{\rm HA} \right)}$$

and solving:

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

This equation is the <u>approximate</u> solution for calculating the [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:

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

Because the A- usually comes from a salt, sometimes the H-H Equation is written in the following form:

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