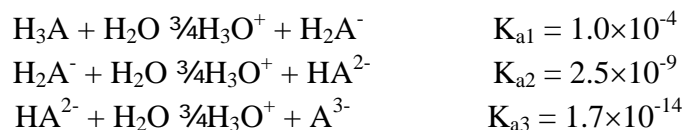


Calculation of concentrations of all species in a polyprotic acid

Let's start off by assuming a general polyprotic acid H_3A with the following ionization equilibria.



We start by calculating the $[H_3O^+]$ and $[H_2A^-]$ from the first equilibrium with an initial concentration of acid of 0.10 M.

$$K_{a1} = \frac{[H_3O^+][H_2A^-]}{[H_3A]} = 1.0 \times 10^{-4}$$

	HA	H_3O^+	A^-
I	0.10	1.0×10^{-7}	0
C	-x	+x	+x
E	$0.10 - x$	$1.0 \times 10^{-7} + x$	x

Making the standard assumptions, we get:

$$K_a = \frac{x^2}{0.10} = 1.0 \times 10^{-4}$$

$$x = \sqrt{(0.10)(1.0 \times 10^{-4})} = 3.2 \times 10^{-3}$$

The assumptions are valid here and we can say that:

$$[H_3O^+] = [H_2A^-] = 3.2 \times 10^{-3} \text{ M}$$

Now we look at the second equilibrium. The values we just calculated are the initial values for the second equilibrium.

$$K_{a2} = \frac{[H_3O^+][HA^{2-}]}{[H_2A^-]} = 2.5 \times 10^{-9}$$

Our ICE table is then:

	H_2A^-	H_3O^+	HA^{2-}
I	3.2×10^{-3}	3.2×10^{-3}	0
C	-x	-x	+x
E	$3.2 \times 10^{-3} + x$	$3.2 \times 10^{-3} + x$	x

Our K in this case is smaller than in the first equilibrium so the x should be smaller than the $[H_3O^+]$. We should be able to neglect x in this case.

$$K_{a2} = \frac{(3.2 \times 10^{-3} + x)(x)}{(3.2 \times 10^{-3} - x)} \approx \frac{(3.2 \times 10^{-3})(x)}{(3.2 \times 10^{-3} x)} = x = 2.5 \times 10^{-9}$$

We see that the doubly ionized form of the acid has a concentration equal to the second K_a .

And now for the third equilibrium:

$$K_{a3} = \frac{[H_3O^+][A^{3-}]}{[HA^{2-}]} = 1.7 \times 10^{-14}$$

In this case the $[H_3O^+]$ is not going to be any different than from the first ionization. Also, the concentration of HA^{2-} is not going to change by much. This is, again, because the K_{a3} is so small. We can then use the previous results to set up the ICE table.

	HA^{2-}	H_3O^+	A^{3-}
I	K_{a2}	3.2×10^{-3}	0
C	-x	-x	+x
E	$K_{a2} + x$	$3.2 \times 10^{-3} + x$	x

Solving the equilibrium gives:

$$K_{a3} = \frac{(3.2 \times 10^{-3} + x)(x)}{(K_{a2} - x)} \approx \frac{(3.2 \times 10^{-3})(x)}{(K_{a2})} = 1.7 \times 10^{-14}$$

$$x = \frac{K_{a2} K_{a3}}{[H_3O^+]} = [A^{3-}]$$

The pH can be found from this information:

$$pH = -\log[H_3O^+] = -\log(3.2 \times 10^{-3}) = 2.50$$

If we have a polyprotic acid with 4 protons the previous is still valid:

$$\begin{aligned} [H_4A]_e &\approx [H_4A]_i \\ [H_3O^+]_e &= [H_3A^-]_e = \sqrt{[H_4A]_i K_{a1}} \\ [H_2A^{2-}]_e &= K_{a2} \\ [HA^{3-}]_e &= \frac{K_{a2} K_{a3}}{[H_3O^+]_e} \\ [A^{4-}]_e &= \frac{K_{a2} K_{a3} K_{a4}}{[H_3O^+]_e^2} \end{aligned}$$

This trend will continue for a pentaprotic and a hexaprotic and so on acid.