

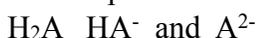
## Fraction of Species

The definition of fraction of species is to first identify ALL the protonated species for a given acid. There are always  $n+1$  species for any acid,  $H_nA$ . The series will look like this:



Realize that it is this very series that will always make up the *material balance* for this particular species.

Now let's consider a diprotic acid,  $H_2A$ . There are 3 total species in the series:



Now, no matter how you go about mixing up a solution containing these species, the TOTAL concentration that you mixed must remain constant - no matter how the species ionize. This is called the *material balance* for this species.

$$\text{Conc mixed} = [H_2A] + [HA^-] + [A^{2-}]$$

Now the fraction of each species (by definition) can be shown to be:

$$f_{H_2A} = \frac{[H_2A]}{[H_2A] + [HA^-] + [A^{2-}]}$$

$$f_{HA^-} = \frac{[HA^-]}{[H_2A] + [HA^-] + [A^{2-}]}$$

$$f_{A^{2-}} = \frac{[A^{2-}]}{[H_2A] + [HA^-] + [A^{2-}]}$$

Once you have the actual values for the fraction of species you can always calculate each individual species by multiplying the fraction of species by the total concentration from the material balance.

$$[H_2A] = f_{H_2A} (\text{total conc})$$

$$[HA^-] = f_{HA^-} (\text{total conc})$$

$$[A^{2-}] = f_{A^{2-}} (\text{total conc})$$

★ Now here is where pages and pages of algebraic substitutions comes in. I will forego all this and go straight to the answers. All those concentrations in the fraction of species equation can be substituted with just  $[H^+]$  and  $K$ 's. By picking a specific pH, you set  $[H^+]$  and the fractions of species are also set. The following polynomial relates directly to the material balance and the fraction of species.

$$[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}$$

Each term in this polynomial is quantitatively relative to the species with as many protons as the term has  $[H^+]$ . So now we have

$$f_{H_2A} = \frac{[H^+]^2}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

$$f_{HA^-} = \frac{K_{a1}[H^+]}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

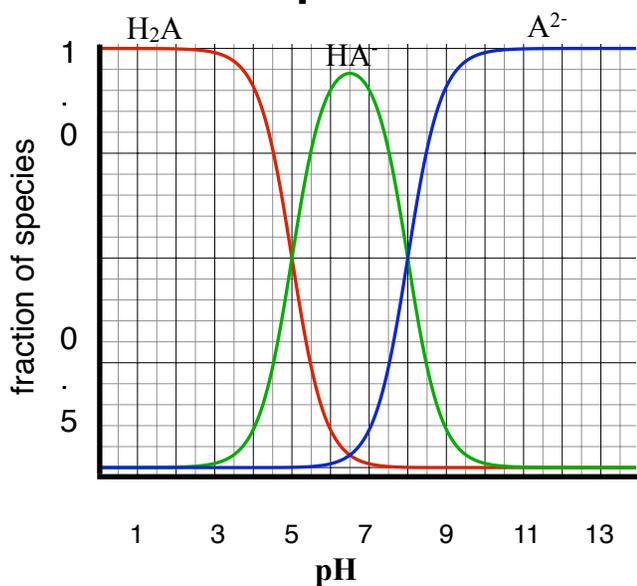
$$f_{A^{2-}} = \frac{K_{a1}K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

Now, armed with these new equations, we can plot the fraction of each species across all possible pH's. Let's have the following  $K_a$  values:

$$K_{a1} = 10^{-5} \quad K_{a2} = 10^{-8}$$

and now the plots

## Fraction of Species



Note how the plots crossover exactly at the  $pK_a$  values (5 and 8 in this case). The green  $HA^-$  line doesn't quite make it all the way back up to 1.0 because the  $K_a$ 's are so close (only 1000x different) that it never makes it to 1.0 for  $f$ . It does peak though at the exact center (average) of the two  $pK_a$ 's surrounding it.

This brings up a nice little formula that comes in very handy for calculating what I call the "sandwiched" species. Those are the species that are neither fully protonated nor fully deprotonated. This are the species on a diagram that rise and then fall in their fractions - just like  $HA^-$  in the above diagram for a diprotic acid. The pH of a solution of the intermediate species will always be the average of the two adjacent  $pK_a$ 's.

$$pH = \frac{pK_{a1} + pK_{a2}}{2}$$

In this formula (and case) the intermediate is the species that has lost ONE proton from the starting polyprotic acid. Realize that the 1 and 2, could also be 2 and 3, or 3 and 4, and so on for polyprotics with many protons.

## Triprotic - $H_3A$

Here is the polynomial for a triprotic acid. Note the sequencing.

$$D = [H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}$$

We will now use  $D$  as our denominator and then take each term in the polynomial and put it in the numerator in order to get each fraction of species.

$$f_{H_3A} = \frac{[H^+]^3}{D} \quad f_{H_2A^-} = \frac{K_{a1}[H^+]^2}{D}$$

$$f_{HA^{2-}} = \frac{K_{a1}K_{a2}[H^+]}{D} \quad f_{A^{3-}} = \frac{K_{a1}K_{a2}K_{a3}}{D}$$

You can apply this same logic (polynomial sequence) for any polyprotic acid with as many protons as needed.

Here is a screen shot of my grapher.app on my mac with the  $K_a$ 's for phosphoric acid. Note that the crossovers are at the  $pK_a$ 's.

