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 this this:

$$H_nA \quad H_{(n-1)}A^- \quad H_{(n-2)}A^{2-} \quad ... \quad A^{-n}$$

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: H_2A HA^- and A^{2-}
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.

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

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

$$f_{H2A} = \frac{[H_2A]}{[H_2A] + [HA^-] + [A^{2-}]}$$

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

$$f_{A2-} = \frac{[A^{2-}]}{[H_2A] + [HA^-] + [A^{2-}]}$$

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.

$$[H_2A] = f_{H2A} \text{ (total conc)}$$
$$[HA^-] = f_{HA-} \text{ (total conc)}$$
$$[A^{2-}] = f_{A2-} \text{ (total conc)}$$

★ 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

$$f_{H2A} = \frac{[H^+]^2}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

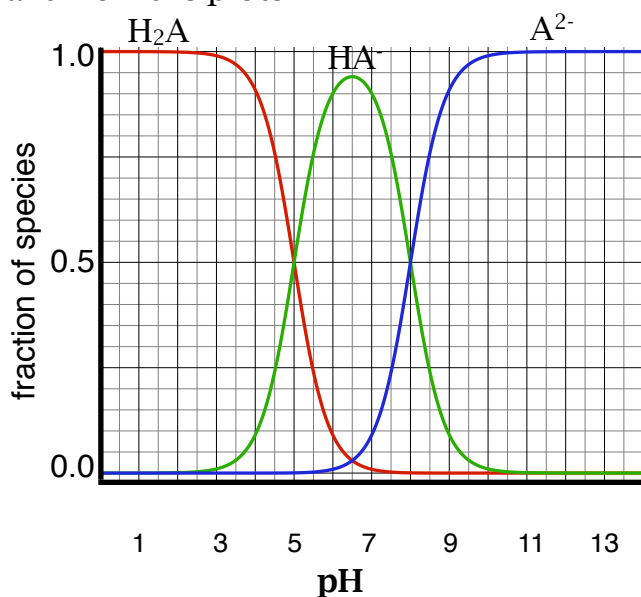$$f_{HA-} = \frac{K_{a1}[H^+]}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

$$f_{A2-} = \frac{K_{a1}K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

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:

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

and now the plots

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 alway 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 - H₃A

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.

$$f_{H3A} = \frac{[H^+]^3}{D} \qquad f_{H2A^-} = \frac{K_{a1}[H^+]^2}{D}$$

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

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