Distribution diagrams are a useful tool to visualize how the balance in concentration between acid and conjugate base varies with pH. *The details of the equations are not important*; what matters are the graphs and how they display what species dominates under what conditions.

Monoprotic acids

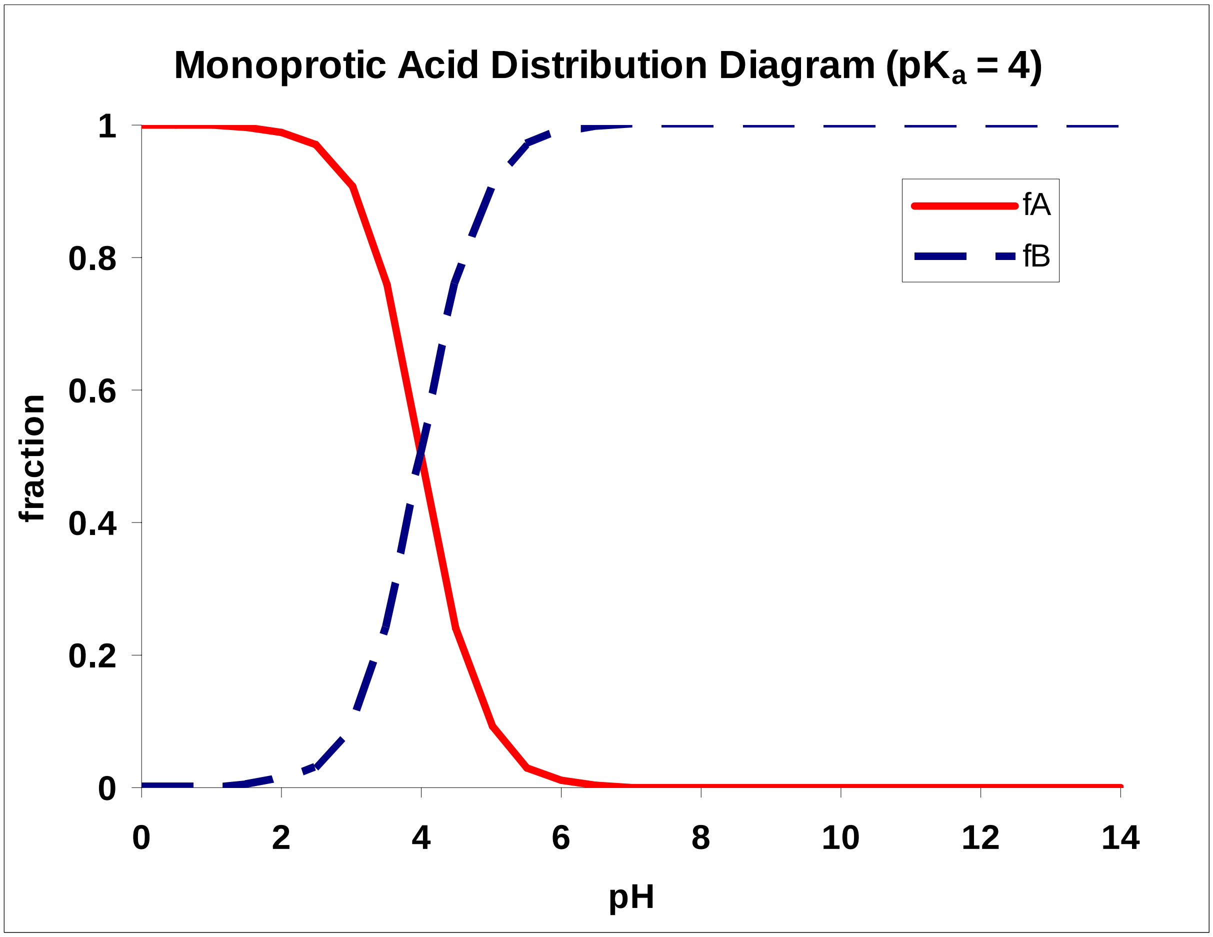
Let $f_B$ = fraction in basic form ($A^-$), and and $f_A$ = fraction in acidic form (HA). Then

$$f_B = [A^-]/\{[A^-]+[HA]\}, \text{ so } 1/f_B = \{[A^-]+ [HA]\}/[A\text{-}] = 1 + [HA]/[A^-]$$

$$K_a = [H^+][A^-]/[HA] \rightarrow [HA]/[A^-] = [H^+]/K_a$$

$$\text{thus } 1/f_B = 1 + [H^+]/K_a = \{K_a + [H^+]\}/K_a \quad \text{invert this:}$$

$$\mathbf{f_B = K_a/\{K_a + [H^+]\}} \text{ and } (1 - f_B) = \mathbf{f_A = [H^+]/\{K_a + [H^+]\}}$$




The shapes of these curves are **the same for all weak acids**; they simply shift left or right, crossing at pH = $pK_a$. Note that the actual concentrations of acid or base do not enter into the final equations: the graphs apply to concentrated and dilute solutions alike!

This graph shows that the two species interconvert over a fairly narrow range of pH. If the pH is more than a couple units from $pK_a$, one or the other species dominates. This can also be inferred from the equation for $K_a$, but the plot may make this easier to visualize. For the above system, with $pK_a = 4$, if the pH is 2 or less, we can say that essentially all the acid is in the form HA, $f_B$ is very small. Conversely, if pH is 6 or greater, essentially all is in the form $A^-$, $f_A$ is very small, less that 1% of the total.

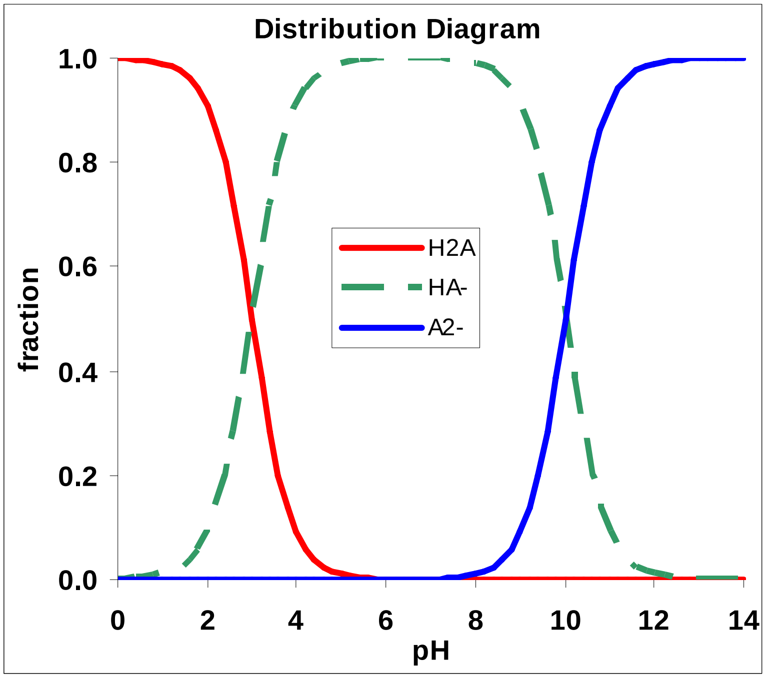
Diprotic Acids. With two hydrolysis reactions with acidity constants $K_{a1}$ and $K_{a2}$, we can write

$$K_{a1} = [H^+][HA^-]/[H_2A] \quad \rightarrow \quad [H_2A]/[HA^-] = [H^+]/K_{a1}$$
$$K_{a2} = [H^+][A^{2-}]/[HA^-] \quad \rightarrow \quad [A^{2-}]/[HA^-] = K_{a2}/[H^+]$$
and
$$K_{a1}\,K_{a2} = [H^+]^2[A^{2-}]/[H_2A] \quad \rightarrow \quad [A^{2-}]/[H_2A] = K_{a1}\,K_{a2}/[H^+]^2$$

Let $f_2$ = fraction in form ($H_2A$), $f_1$ = fraction in form ($HA^-$), and $f_0$ = fraction in form ($A^{2-}$).

$$f_2 = [H_2A]/\{[H_2A] + [HA^-] + [A^{2-}]\}$$
$$1/f_2 = \{[H_2A] + [HA^-] + [A^{2-}]\}/[H_2A] = 1 + [HA^-]/[H_2A] + [A^{2-}]/[H_2A]$$
$$= 1 + K_{a1}/[H^+] + K_{a1}K_{a2}/[H^+]^2 = \{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}\}/[H^+]^2$$

invert to find $f_2$; similar derivations for $f_1$ and $f_0$. Look at two cases.



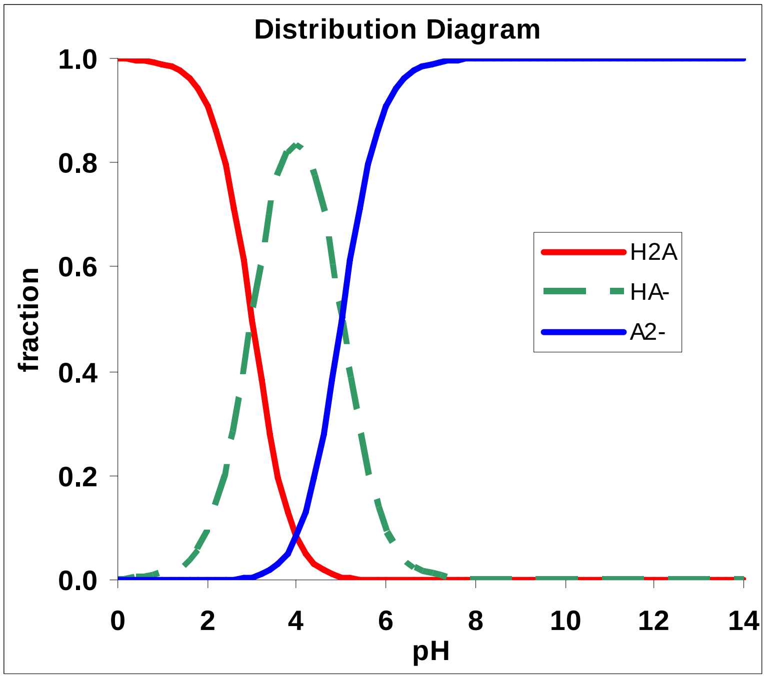

First, consider a diprotic acid with non-overlapping stages of ionization: $K_{a1}$ and $K_{a2}$ differ by a lot (factor of 10,000 or more; pK's differ by 4 or more). Here $pK_{a1} = 3$ and $pK_{a2} = 10$.

This plot resembles two monoprotic acids: one changes from acidic to basic over the range pH 1 to 5 (crossing at 3), the other changes over the range 8 to 12 (crossing at 10).

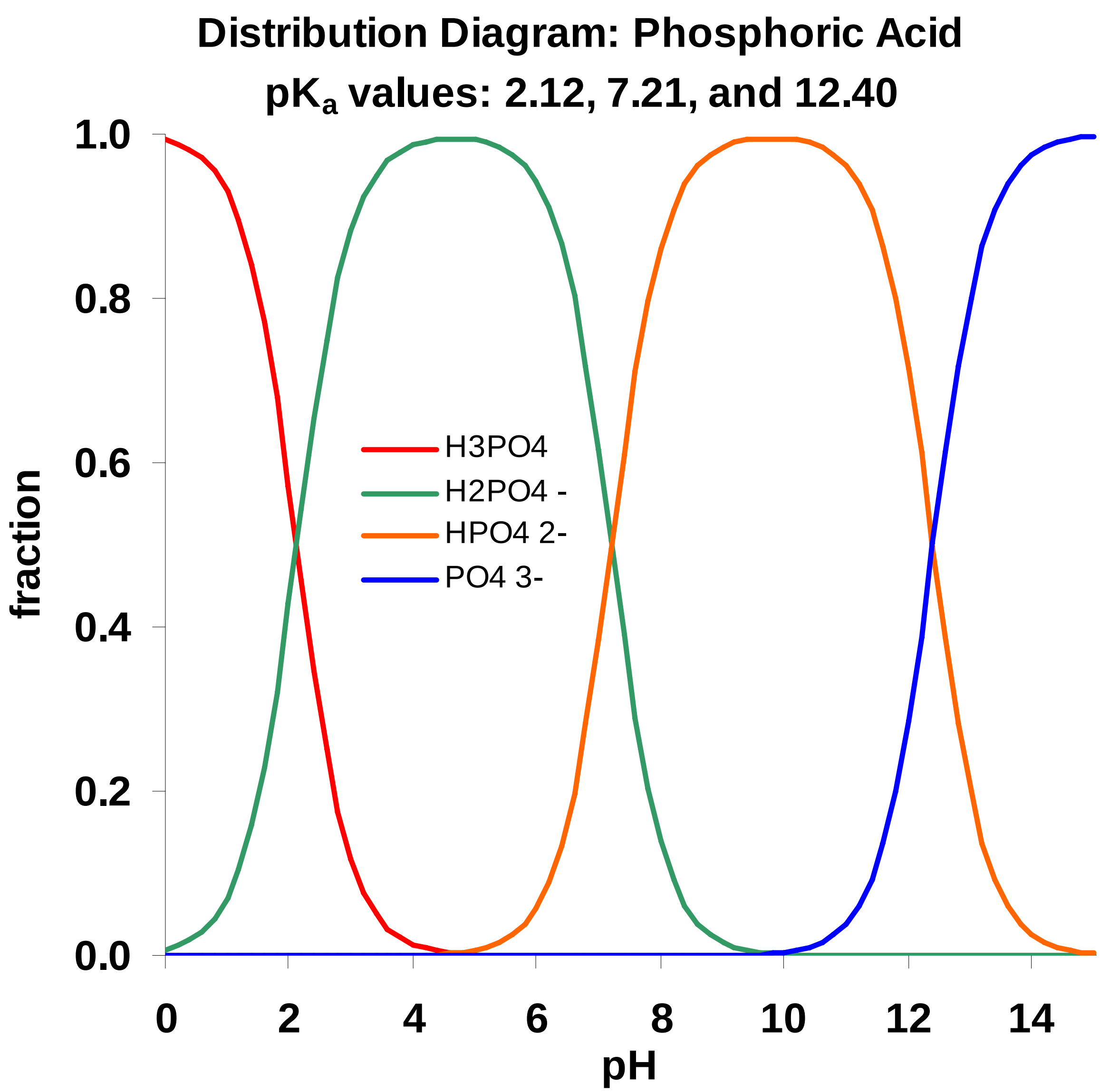
In other words, the first ionization step is essentially complete before the second one starts. This is why in a titration of such an acid, there is a distinct jump in pH at $V_{1e}$.

Compare with an acid with $K_{a1}$ and $K_{a2}$ not very far apart; here they differ by a factor of 100 ($pK_{a1} = 3$ and $pK_{a2} = 5$). The curves again cross at $pK_{a1}$ and $pK_{a2}$. What differs is that before the $H_2A$ fraction has fallen close to zero, the $A^{2-}$ fraction has begun to rise. This is why there is not a steep jump at $V_{1e}$.

For pH between about 3 and 5, all three species are present in significant amounts. But as above, when the pH is a couple units to the acidic side of $pK_{a1}$, essentially all is in the form $H_2A$, whereas when the pH is a couple of units to the basic side of $pK_{a2}$, it is essentially all $A^{2-}$.



<u>Triprotic Acid</u>. There is a very important triprotic acid, **phosphoric acid**, $H_3PO_4$. The three $pK_a$ values are quite different (approximately 2, 7, and 12) so that there is little overlapping behavior. At pH values near 7, the concentrations of $H_2PO_4^-$ [green] and $HPO_4^{2-}$ [orange] are much much larger that both $H_3PO_4$ [red] and $PO_4^{3-}$ [blue]. (A logarithmic diagram may be helpful to see the difference; see the following page.) Phosphate buffers, of widespread use in biology and biochemistry, have pH values between 6 and 8, depending on the relative amount of $H_2PO_4^-$ and $HPO_4^{2-}$ . To calculate the pH, one can use $K_{a2}$ exclusively: this diagram shows that the loss of the first proton, described by $K_{a1}$, is essentially complete, and the loss of the last proton, described by $K_{a3}$, has yet to begin.



**Logarithmic Distribution Diagram for Phosphoric Acid**

(the y-axis shows the base-10 logarithm of the fraction). Observe that at pH =6, the fraction of acid in the form $H_3PO_4$ is less that $10^{-4}$, while that of $PO_4^{3-}$ is about $10^{-8}$. It is therefore an excellent approximation to say that these are negligible.