CONCEPT: FRACTIONAL COMPOSITION

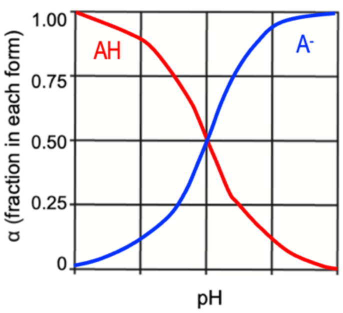
Fractional compositions are used as an illustration for the amount of acid or base species at a specific pH.

Monoprotic Systems

The dissociation of a weak monoprotic acid creates an equilibrium and expression that can be tied to its mass balance.

$$HA \rightleftharpoons H^+ + A^- \qquad K_a = \frac{[H^+][A^-]}{[HA]} \qquad \text{Mass Balance}: F = [HA] + [A^-]$$

The fraction of HA molecules is represented by α_{HA}.



$$[HA] = \frac{[H^+]F}{[H^+] + K_a} \xrightarrow{\text{Dividing by F}} \alpha_{HA} = \frac{HA}{F} = \frac{[H^+]}{[H^+] + K_a}$$

The fraction in the conjugate base form, A⁻, can be represented as α_{A^-}.

$$\alpha_{A^-} = \frac{A^-}{F} = \frac{K_a}{[H^+] + K_a}$$

Diprotic Systems

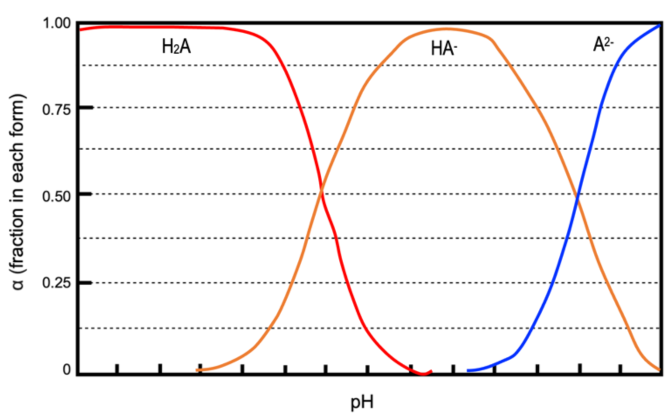
From the derived equilibrium expressions we can determine the mass balance.

$$H_2A \rightleftharpoons H^+ + HA^- \qquad K_{a_1} = \frac{[H^+][HA]}{[H_2A]} \Rightarrow [HA^-] = \frac{[H_2A][K_{a_1}]}{[H^+]}$$

$$HA^- \rightleftharpoons H^+ + A^{2-} \qquad K_{a_2} = \frac{[H^+][A^{2-}]}{[HA^-]} \Rightarrow [A^{2-}] = \frac{[HA^-][K_{a_2}]}{[H^+]} = \frac{[H_2A]K_{a_1}K_{a_2}}{[H^+]^2}$$

$$F = [H_2A]\left[[H_2A]\cdot\frac{[H^+]^2 + [H^+]K_{a_1} + K_{a_1}K_{a_2}}{[H^+]^2}\right]$$

The fractions of the three major diprotic forms can be seen as:



$$\alpha_{H_2A} = \frac{H_2A}{F} = \frac{[H^+]^2}{[H^+]^2 + [H^+]K_{a_1} + K_{a_1}K_{a_2}}$$

$$\alpha_{HA^-} = \frac{HA^-}{F} = \frac{K_{a_1}[H^+]}{[H^+]^2 + [H^+]K_{a_1} + K_{a_1}K_{a_2}}$$

$$\alpha_{A^{2-}} = \frac{A^{2-}}{F} = \frac{K_{a_1}K_{a_2}}{[H^+]^2 + [H^+]K_{a_1} + K_{a_1}K_{a_2}}$$

PRACTICE: FRACTIONAL COMPOSITION

EXAMPLE 1: A dibasic compound, B, has pK_{b1} = 5.00 and pK_{b2} = 8.00. Find the fraction of the acidic form when the pH = 9.00.

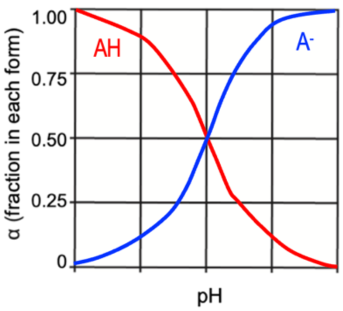
EXAMPLE 2: What fraction of tyrosine (pK_{a1} = 2.37, pK_{a2} = 8.67) exists in all of its forms at pH = 10.00?

PRACTICE: Calculate the fraction of the intermediate for sulfurous acid, H_2SO_3, at pH = 11.00? pK_{a1} = 1.80, pK_{a2} = 7.19.

CONCEPT: FRACTIONAL COMPOSITION

Monoprotic Systems

Recall that the fraction of HA and A^- molecules are represented by α_{HA^-} and α_{A^-}.



$$\alpha_{HA} = \frac{HA}{F} = \frac{[H^+]}{[H^+]+K_a}$$

$$\alpha_{A^-} = \frac{A^-}{F} = \frac{K_a}{[H^+]+K_a}$$

When taking into account the formal concentrations of HA and A^- molecules we now restructure the equations:

$$[HA] = \alpha_{HA}F_{HA} = \frac{[H^+]F_{HA}}{[H^+]+K_a}$$

$$[A^-] = \alpha_{A^-}F_{HA} = \frac{K_aF_{HA}}{[H^+]+K_a}$$

Diprotic Systems

From the derived equilibrium expressions we can determine the mass balance.

$$H_2A \rightleftharpoons H^+ + HA^-$$

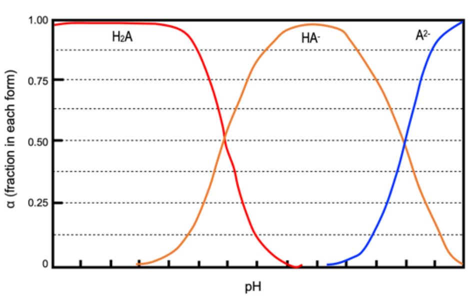
$$K_{a_1} = \frac{[H^+][HA]}{[H_2A]} \Rightarrow [HA^-] = \frac{[H_2A][K_{a_1}]}{[H^+]}$$

$$HA^- \rightleftharpoons H^+ + A^{2-}$$

$$K_{a_2} = \frac{[H^+][A^{2-}]}{[HA^-]} \Rightarrow [A^{2-}] = \frac{[HA^-][K_{a_2}]}{[H^+]} = \frac{[H_2A]K_{a_1}K_{a_2}}{[H^+]^2}$$

$$F = [H_2A]\left[[H_2A]\cdot\frac{[H^+]^2+[H^+]K_{a_1}+K_{a_1}K_{a_2}}{[H^+]^2}\right]$$

The formal concentrations of the three major diprotic forms can be restructured as:



$$\alpha_{H_2A} = \frac{H_2A}{F} = \frac{[H^+]^2}{[H^+]^2+[H^+]K_{a_1}+K_{a_1}K_{a_2}}$$

$$[H_2A] = \alpha_{H_2A}F_{H_2A} = \frac{[H^+]^2F_{H_2A}}{[H^+]^2+[H^+]K_{a_1}+K_{a_1}K_{a_2}}$$

$$\alpha_{HA^-} = \frac{HA^-}{F} = \frac{K_{a_1}[H^+]}{[H^+]^2+[H^+]K_{a_1}+K_{a_1}K_{a_2}}$$

$$[HA^-] = \alpha_{HA^-}F_{H_2A} = \frac{K_{a_1}[H^+]F_{H_2A}}{[H^+]^2+[H^+]K_{a_1}+K_{a_1}K_{a_2}}$$

$$\alpha_{A^{2-}} = \frac{A^{2-}}{F} = \frac{K_{a_1}K_{a_2}}{[H^+]^2+[H^+]K_{a_1}+K_{a_1}K_{a_2}}$$

$$[A^{2-}] = \alpha_{A^{2-}}F_{H_2A} = \frac{K_{a_1}K_{a_2}F_{H_2A}}{[H^+]^2+[H^+]K_{a_1}+K_{a_1}K_{a_2}}$$

PRACTICE: FRACTIONAL COMPOSITION

EXAMPLE 1: A dibasic compound, B, has pK_{b1} = 4.00 and pK_{b2} = 6.00. Find the concentration of the intermediate form when F_{H_2A} = 0.150 M and the pH = 8.00.

EXAMPLE 2: Calculate the concentration of the acidic form for 0.230 M tartaric acid, $H_2C_4H_4O_6$, at pH = 6.00? pK_{a1} = 3.00, pK_{a2} = 4.34.