Zwitterion behavior of an amino acid.
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An amino acid acts as a zwitterion, i.e., it can be either:
1) a positively charged cation (A^+) in an acid solution,
2) a negatively charged anion (A^-) in an alkaline solution, or
3) a neutral molecule (A) at the isoelectric point.

Zwitterion Reaction:

NH_3^+-CHR-COOH ⟶ NH_3^+-CHR-COO$^-$ + H^+

NH_3^+-CHR-COO$^-$ ⟶ NH_2-CHR-COO$^-$ + H^+

which can be abbreviated as:

$A^+ \longrightarrow A + H^+ \qquad K_1$

$A \longrightarrow A^- + H^+ \qquad K_2$

The dissociation constants for these steps are K_1 and K_2, which are defined as:

$$pK_1 = -\log(K_1) = -\log\left(\frac{A_{neutral} \cdot H}{A_{cation}}\right) \qquad pK_2 = -\log(K_2) = -\log\left(\frac{A_{anion} \cdot H}{A_{neutral}}\right)$$

Below, we shall let Mathcad find how amino acid exists in a solution (via |Math|SmartMath|).

$$\text{Given} \qquad \frac{A_{neutral} \cdot H}{A_{cation}} = 10^{-pK_1} \qquad \frac{A_{anion} \cdot H}{A_{neutral}} = 10^{-pK_2}$$

Conservation of mass (i.e., all fractions add up to unity): $A_{cation} + A_{neutral} + A_{anion} = 1$

We have three equations and we can solve for any three unknowns.

$$\text{Find}(A_{cation}, A_{neutral}, A_{anion}) \rightarrow \begin{bmatrix} \dfrac{H^2}{\left[H^2 + H \cdot 10^{(-pK_1)} + 10^{(-pK_2)} \cdot 10^{(-pK_1)}\right]} \\ H \cdot \dfrac{10^{(-pK_1)}}{\left[H^2 + H \cdot 10^{(-pK_1)} + 10^{(-pK_2)} \cdot 10^{(-pK_1)}\right]} \\ 10^{(-pK_2)} \cdot \dfrac{10^{(-pK_1)}}{\left[H^2 + H \cdot 10^{(-pK_1)} + 10^{(-pK_2)} \cdot 10^{(-pK_1)}\right]} \end{bmatrix}$$

Copy the above analytical formula to the functions below, and substitute the definition of pH. $H = 10^{-pH}$

$$A_{cation}(pH, pK_1, pK_2) := \frac{\left(10^{-pH}\right)^2}{\left(10^{-pH}\right)^2 + 10^{-pK_1} \cdot 10^{-pH} + 10^{-pK_1} \cdot 10^{-pK_2}}$$

$$A_{neutral}(pH, pK_1, pK_2) := \frac{10^{-pK_1} \cdot 10^{-pH}}{\left(10^{-pH}\right)^2 + 10^{-pK_1} \cdot 10^{-pH} + 10^{-pK_1} \cdot 10^{-pK_2}}$$

$$A_{anion}(pH, pK_1, pK_2) := \frac{10^{-pK_1} \cdot 10^{-pK_2}}{\left(10^{-pH}\right)^2 + 10^{-pK_1} \cdot 10^{-pH} + 10^{-pK_1} \cdot 10^{-pK_2}}$$

Example: Alanine has the following dissociation constants: $pK_1 := 2.34$ $pK_2 := 9.69$

in a neutral solution: $pH := 7$

$$A_{cation}(pH, pK_1, pK_2) = 2.183 \cdot 10^{-5}$$

$$A_{neutral}(pH, pK_1, pK_2) = 0.998$$ ← Amino acid exists mostly as a neutral molecule.

$$A_{anion}(pH, pK_1, pK_2) = 0.002$$

in an acid solution: $pH := 1$

$$A_{cation}(pH, pK_1, pK_2) = 0.956$$ ← Amino acid exists mostly as a cation A^+.

$$A_{neutral}(pH, pK_1, pK_2) = 0.044$$

$$A_{anion}(pH, pK_1, pK_2) = 8.925 \cdot 10^{-11}$$

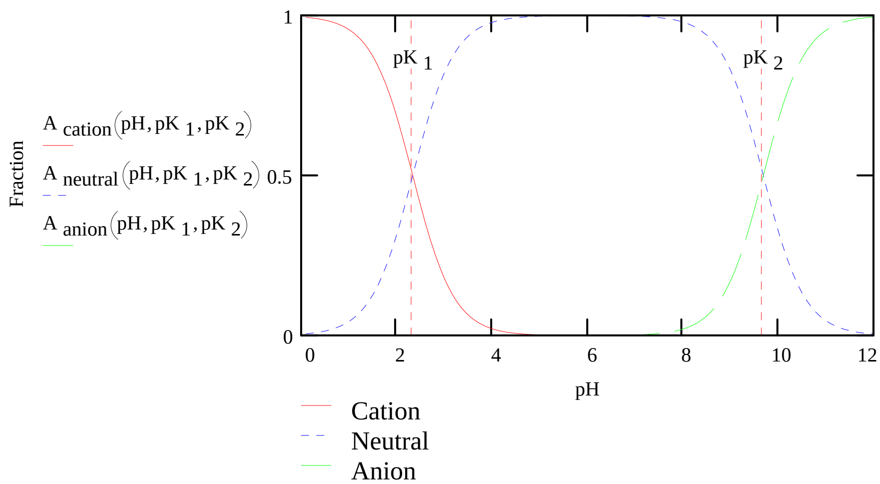
in an alkaline solution: $pH := 11$

$$A_{cation}(pH, pK_1, pK_2) = 1.021 \cdot 10^{-10}$$

$$A_{neutral}(pH, pK_1, pK_2) = 0.047$$

$$A_{anion}(pH, pK_1, pK_2) = 0.953$$ ← Amino acid exists mostly as an anion A^-.

Plot pH dependence for a range of pH values: $pH := 0.1, 0.2 .. 12$



At $pH=(pK_1+pK_2)/2$ (i.e., midway between two pK's), the zwitterion is mostly neutral. At $pH=pK_1$ or $pH=pK_2$ the fraction of the respective species involved is about half.