

Fractional Composition Equations

Why determine fractional compositions?

- Fractional composition clearly show the dominant and minor species in solution.
- Fractional compositions provide a way to know what reactions are occurring, and what reactions are relatively unimportant.
- Fractional compositions make really cool plots.

Monoprotic Systems

For an acid -

$$\alpha_{\text{HA}} = [\text{HA}] / F$$

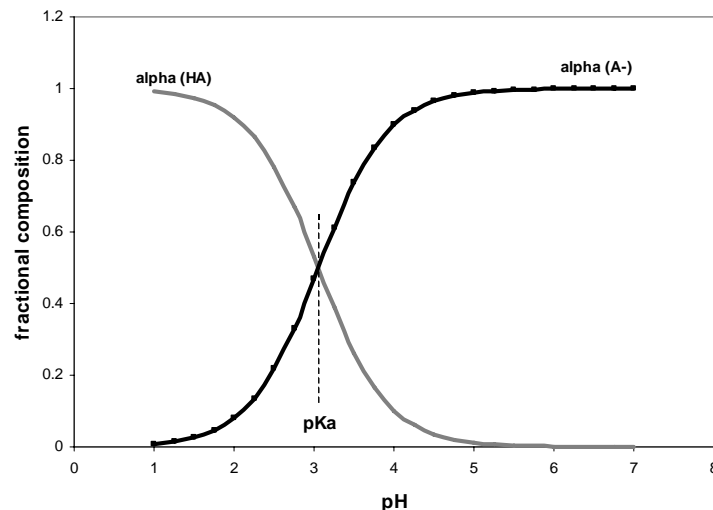
$$\alpha_{\text{A}^-} = [\text{A}^-] / F$$

For a base -

$$\alpha_{\text{b}} = [\text{B}] / F$$

$$\alpha_{\text{BH}^+} = [\text{BH}^+] / F$$

$F = \text{Formal concentration}$



Diprotic Systems

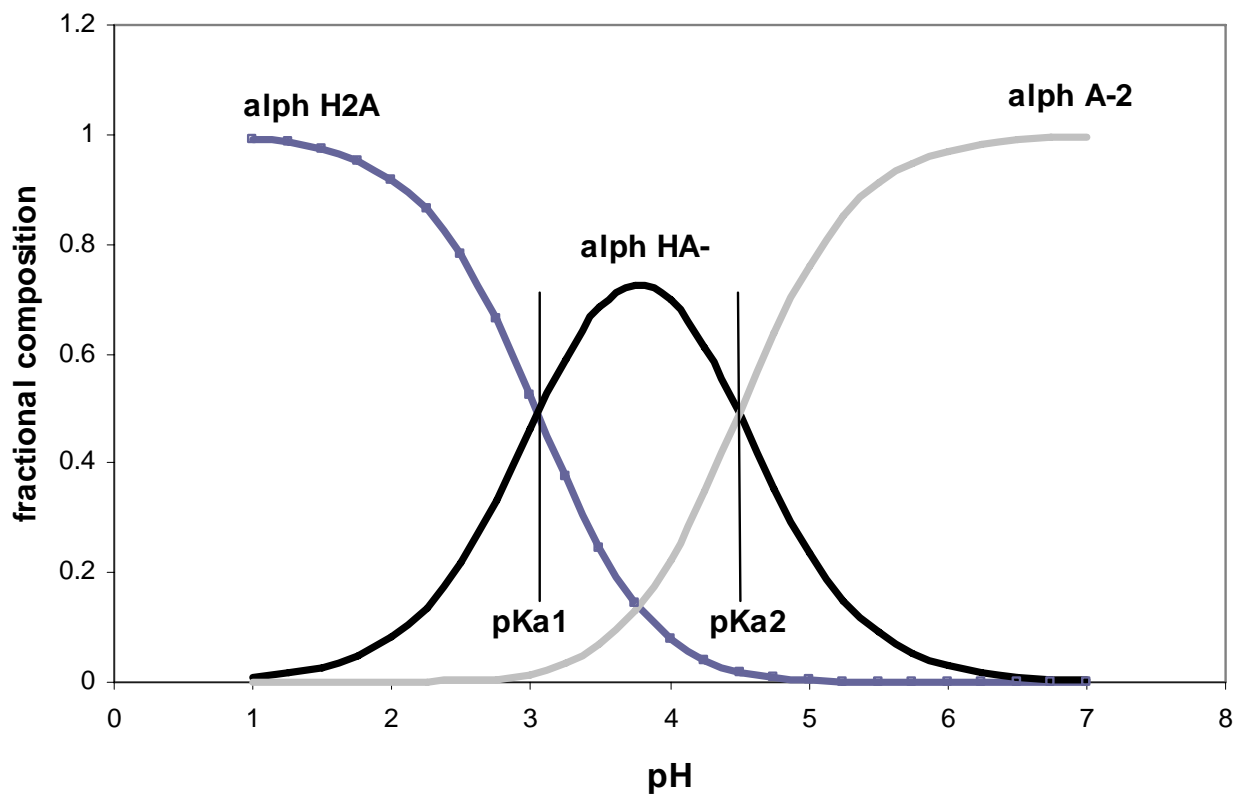
For an acid -

$$\alpha_{\text{H}_2\text{A}} = [\text{H}_2\text{A}] / F$$

$$\alpha_{\text{HA}^-} = [\text{HA}^-] / F$$

$$\alpha_{\text{A}^{2-}} = [\text{A}^{2-}] / F$$

F = Formal concentration



Calculating Fractional Compositions from $[H^+]$ and K_a 's

For an acid – H_2A :

$$\alpha_{H_2A} = [H_2A] / F$$

$$\alpha_{HA^-} = [HA^-] / F$$

$$\alpha_{A^{2-}} = [A^{2-}] / F$$

F = Formal concentration

$$\alpha_{H_2A} = [H^+]^2 / D$$

$$\alpha_{HA^-} = [H^+] K_{a1} / D \quad \text{where } D = [H^+]^2 + [H^+] K_{a1} + K_{a1} K_{a2}$$

$$\alpha_{A^{2-}} = K_{a1} K_{a2} / D$$

Biochemical terms

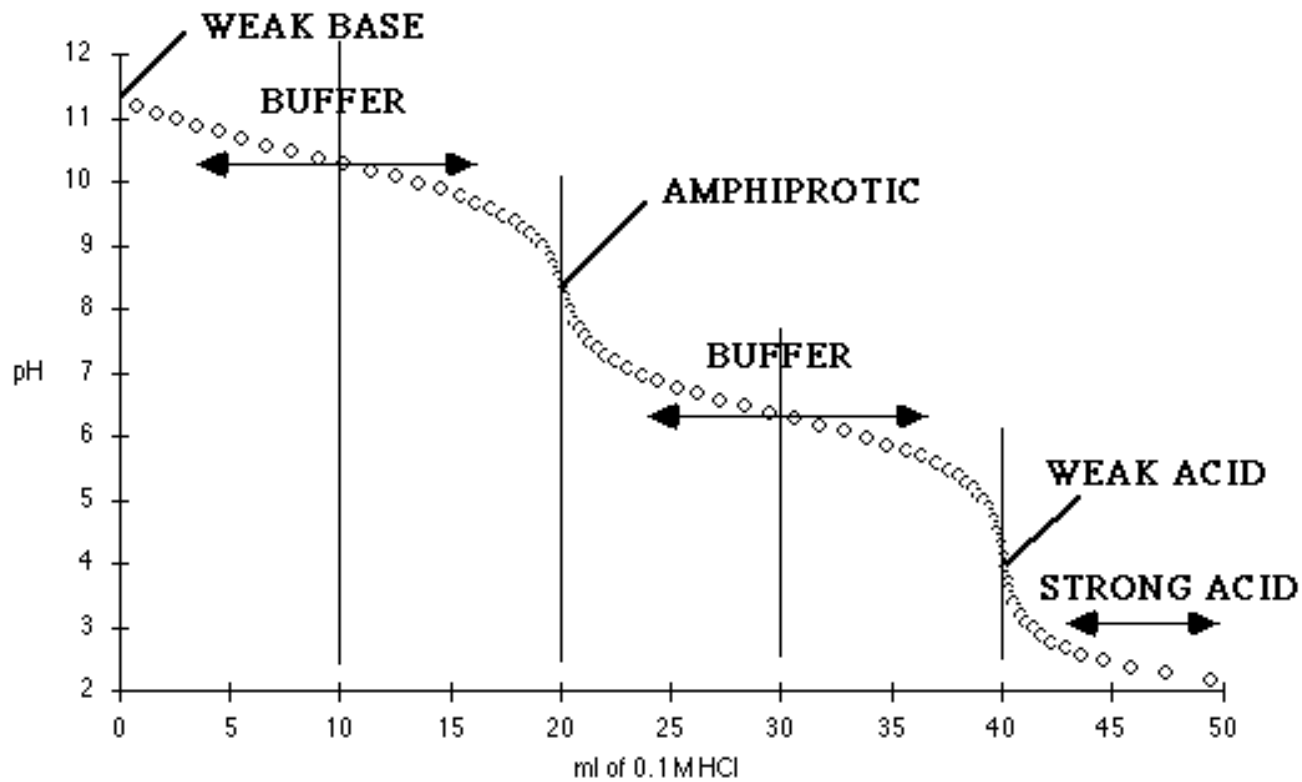
Isoionic pH : pH of a solution where the pure, neutral polyprotic acid has been dissolved.

Isoelectric pH : pH of a solution when the average charge on the polyprotic acid is 0.

The isoelectric pH is useful for separating various polyprotic acids from one another. If you put these acids in a electric field and a pH gradient, they will focus themselves in a region of the pH corresponding to their isoelectric pH (they do not move toward the positive or negative pole).

Diprotic Buffers – treated similar to a monoprotic buffer. You must know what the desired pH and the appropriate pKa are.

$$\text{pH} = \text{pKa} + \log \frac{[\text{base}]}{[\text{acid}]}$$

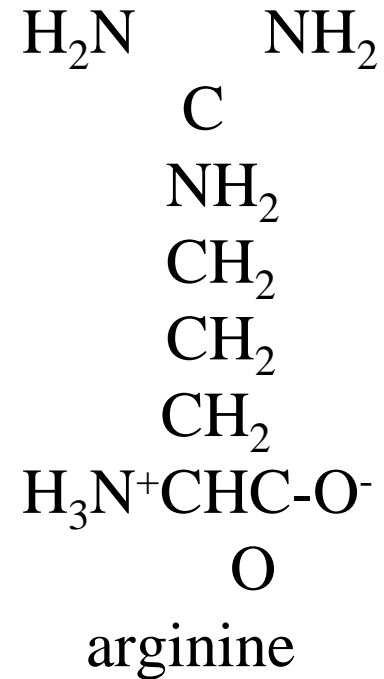
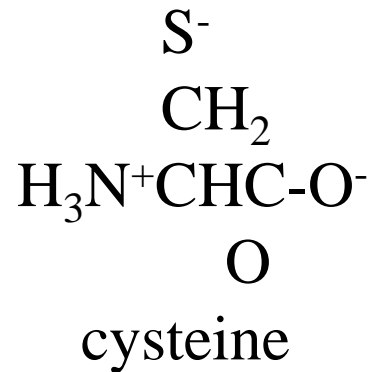
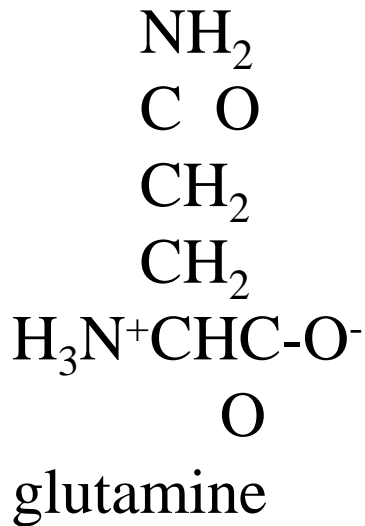


Buffer problem

How many grams of NaHCO_3 (FM 84.007) must be added to 4.00 g of K_2CO_3 (FM 138.206) to give a pH of 10.80 in 500 mL of water?

What will be the pH if 100 mL of 0.1 M HCl are added to above solution?

Calculate the pH of a 0.10 M solution of each amino acid.



Draw the structure and the fractional composition of the principal species of 1,3-dihydroxybenzene at the following pH values:

$$(\text{pK}_{\text{a}1} = 9.40 \quad \text{pK}_{\text{a}2} = 12.8)$$

pH 9

pH 11