Activity #2: Alpha Fractions: A Useful Way to Solve Acid/Base Problems

Alpha fractions are defined as the fractional amount of acid that exists in a certain form. The total amount of an acid added to a solution is called either the analytical concentration (C_A) or the formal concentration (F_A) of the acid. Thus, if 0.100 M acetic acid is added to a solution, $C_A = F_A = 0.100$ M, no matter what the ratio of the acid and its conjugate base. The actual concentrations of the dissociated and undissociated forms are denoted as the equilibrium concentrations and written with the usual symbols ($[A^-]$ and $[HA]$).

Let's look at how the alpha fraction works for a simple monoprotic weak acid. We define α_{HA} as the fraction of C_A that exists as HA and α_A as the fraction that exists as A^-. The fractions are written as follows:

$$\alpha_{A^-} = \frac{[A^-]}{[HA] + [A^-]} \qquad \alpha_{HA} = \frac{[HA]}{[HA] + [A^-]}$$

$$\alpha_{A} = \frac{[A^-]}{C_A} \qquad \alpha_{HA} = \frac{[HA]}{C_A}$$

1) Write a reaction for the dissociation of the generic acid, HA, in water.

2) Write an expression for the acid dissociation constant, K_a, for HA in terms of equilibrium molar concentrations.

3) Solve for $[A^-]$ in terms of $[HA]$, $[H_3O^+]$ and K_a.

4) Using this derived expression for $[A^-]$, solve for α_A in terms of $[HA]$, $[H_3O^+]$ and K_a only.

5) Now, eliminate [HA] from the previous expression and solve for the alpha fraction for A^- in terms of K_a and $[H_3O^+]$ only.

6) If you've done this correctly, you should be able to simplify your expression to the following:

$$\alpha_{A^-} = \frac{K_a}{K_a + [H_3O^+]}$$

Because the fractions of HA + A^- must add up to equal 1:

$$\alpha_{HA} + \alpha_{A^-} = 1$$

7) Using this knowledge, derive an expression for α_{HA} in terms of K_a and $[H_3O^+]$ only (there should be no "1" in the answer when you have simplified the expression).

These are general expressions for any monoprotic acid.

8) When $[H_3O^+] = K_a$ what are the values of α_{A-} and α_{HA}? Does your answer make sense?

9) Complete the following by simply adding the missing term:

$$[A^-] = \alpha_{A-} * \_\_\_\_$$

$$[HA] = \alpha_{HA} * \_\_\_\_$$

Graphing Alpha Fractions vs. pH

It is easiest to display data in a log format. This is usually done by graphing logα (y-axis) vs. pH (x-axis).

10) Solve for log α_{HA} in terms of pH, K_a and $[H_3O^+]$.

11) Solve for log α_A in terms of pK_a, K_a and $[H_3O^+]$.

12) Solve for log α_{A-} and log α_{HA} in terms of p K_a and pH when $K_a >> [H_3O^+]$.

13) Solve for log α_{A-} and log α_{HA} in terms of pK_a and pH when $K_a << [H_3O^+]$.

14) What are the slope and y-intercept of a plot of log α_{A-} vs. pH and log α_{HA} vs. pH in the two regions ($K_a << [H_3O^+]$ and $K_a >> [H_3O^+]$) of the graph?

15) On a 1 mm ruled graph paper, plot both of the dependent variables, log α_{A-} and log α_{HA} vs. pH (independent variable). Use a y-scale of 0 to -14 and an x scale from 0-14.

16) On the same graph, plot the log $[H_3O^+]$ vs pH and log $[OH^-]$ vs. pH using the expression $K_W = [H_3O^+] [OH^-]$ or from your knowledge of the relation between pH and log $[H_3O^+]$, and between pOH and log $[OH^-]$.

17) There are three principal intercepts on the graph. Circle the intercepts and solve for pH at each intercept. Each of these intercepts represents an important point in a titration. Identify each titration point.

Polyprotic Acids

We can derive the alpha fractions for a diprotic acid in a similar manner. The only difference is that we now have three terms to consider ($[H_2A]$, $[HA^-]$ and $[A^{2-}]$). The denominator will still be the analytical concentration, but this time we must derive each concentration in terms of two K_a 's and the $[H_3O^+]$. The expressions for the three alpha fractions are:

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

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

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

The results of the derivations for a diprotic acid are the following expressions:

$$\alpha_{H_2A} = \frac{[H_3O^+]^2}{[H_3O^+]^2 + K_1[H_3O^+] + K_1K_2}$$

$$\alpha_{HA^-} = \frac{K_1[H_3O^+]}{[H_3O^+]^2 + K_1[H_3O^+] + K_1K_2}$$

$$\alpha_{A^{2-}} = \frac{K_1K_2}{[H_3O^+]^2 + K_1[H_3O^+] + K_1K_2}$$

Problem: Using your powers of induction from the monoprotic and diprotic acids, derive the alpha fraction expressions for a triprotic acid in terms of the equilibrium constants and $[H_3O^+]$ only. You will need these for the spreadsheet exercise.