Titration of Polyprotic Acids

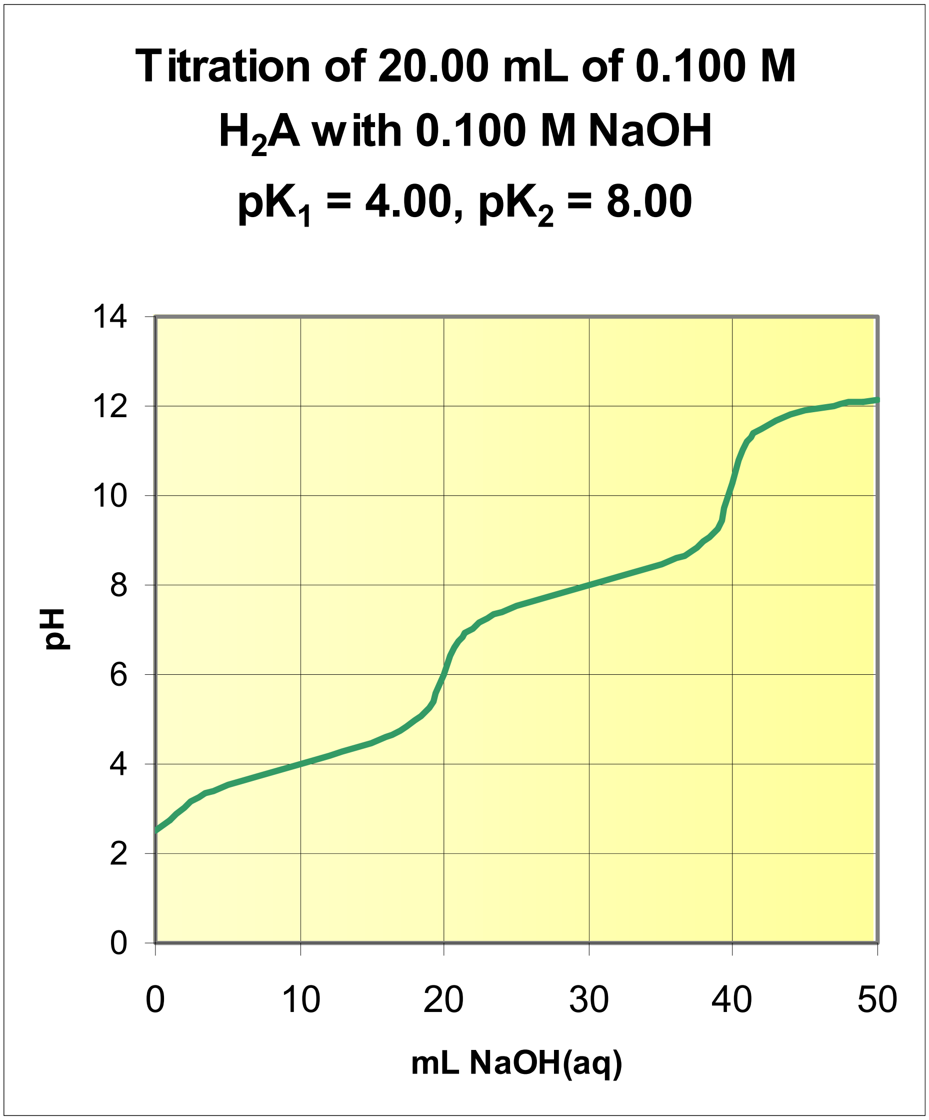
- ✔ The shape of the titration curve for a polyprotic acid reflects the successive neutralization of the two or more ionizable hydrogen atoms in its formula.

- ✔ If the successive K_a values are numerically widely separated, the titration can be regarded as occurring in a stepwise manner, with the first hydrogen being neutralized before the second, and so forth:

$$H_2A + OH^- \rightarrow HA^- + H_2O$$
$$HA^- + OH^- \rightarrow A^{2-} + H_2O$$

- ✔ If the successive K_a values are widely separated, the titration curve shows a break for each proton's neutralization.

Titration of an Ideal Diprotic Acid



Calculation of pH
First Equivalence Point

☹ The calculation of pH vs. mL of titrant added is not straightforward in many polyprotic acid cases and is beyond the scope of this course.

✔ Volume of titrant needed to reach the first equivalent point is calculated in the same manner as for a monoprotic acid; i.e., $V_b = V_a M_a / M_b$.

- At this point, all the H_2A initially present has been converted into HA^-.
- pH at this point is governed by the competing tendencies of the acid anion HA^- to function both as an acid and a base; i.e., its amphiprotic nature.

✔ In simple cases where the acid and base tendencies of HA^- are roughly equal, pH at the first equivalence point is *approximately* the average of the two pK_a values.

Calculation of pH
Second Equivalence Point

- ✔ An additional volume of titrant, equal to that needed to reach the first equivalence point, must be added to reach the second equivalence point.

- ✔ At the second equivalence point all the HA^- has been converted into A^{2-}, and pH can be calculated as for a solution of Na_2A, for which $K_b = K_w/K_2$.

- ✔ For cases with widely separated K_a's, pH at each half-equivalence point is the pK_a of the species being neutralized.