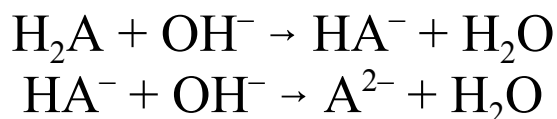


Titration of Polyprotic Acids

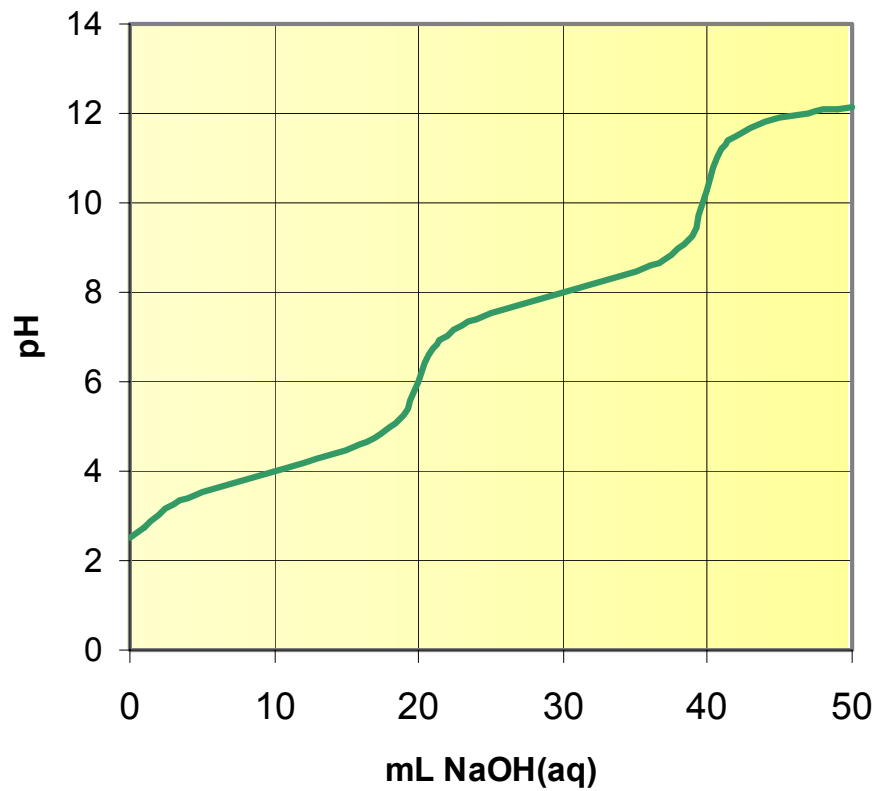
- ✓ The shape of the titration curve for a polyprotic acid reflects the successive neutralization of the two or more ionizable hydrogen atoms in its formula.
- ✓ If the successive K_a values are numerically widely separated, the titration can be regarded as occurring in a stepwise manner, with the first hydrogen being neutralized before the second, and so forth:



- ✓ 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

Titration of 20.00 mL of 0.100 M
 H_2A with 0.100 M NaOH
 $\text{pK}_1 = 4.00$, $\text{pK}_2 = 8.00$



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 amphoteric 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 $\text{p}K_a$ of the species being neutralized.