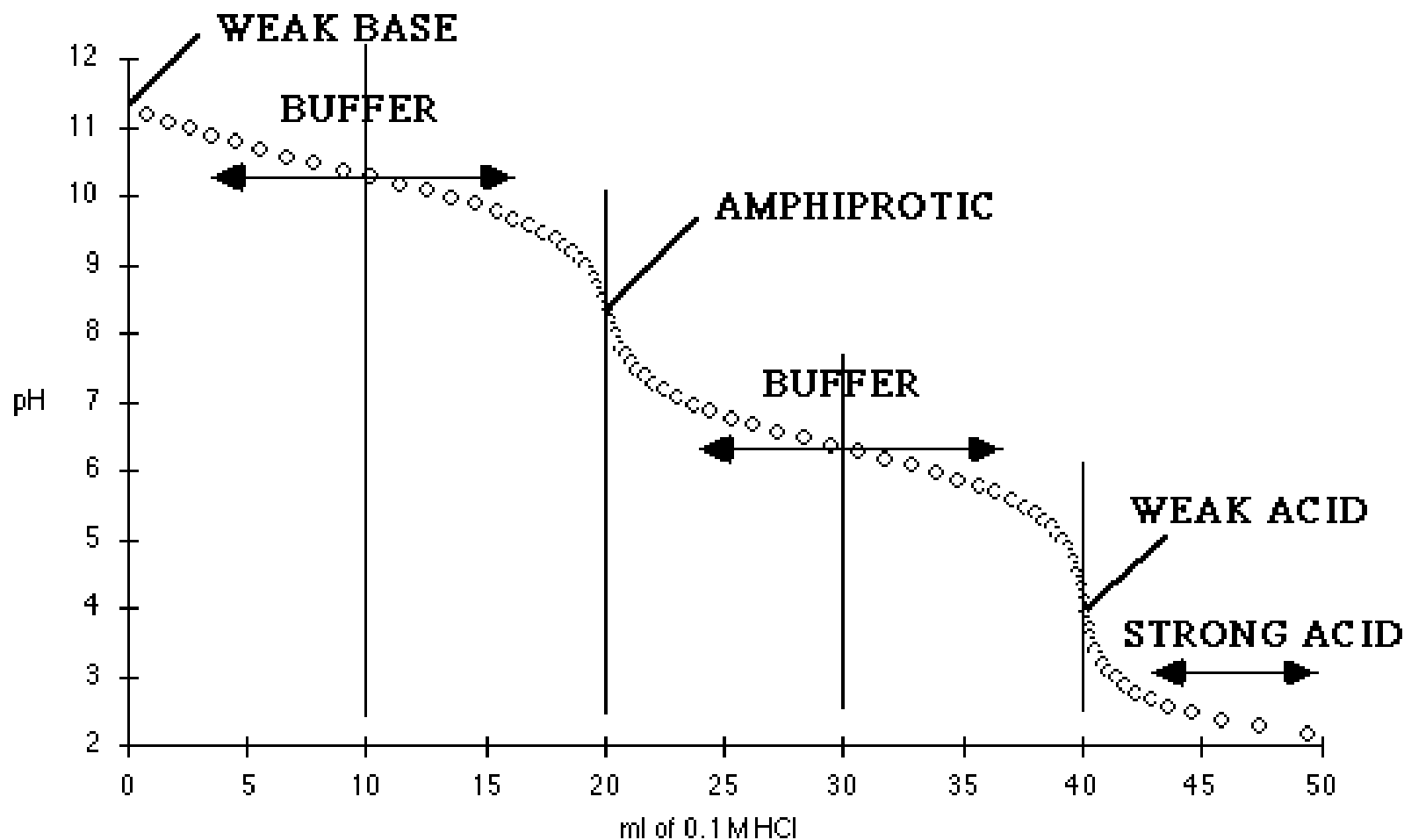


Chapter 11 - Polyprotic Acid-Base Equilibria (continued)

Titration of Polyprotic Base with Strong Acid

Titration of 2 mm of Na_2CO_3 with 0.1 M HCl



Polyprotic Acids



$$K_{a1} = \frac{[\mathbf{H^+}][\mathbf{H_2A^-}]}{[\mathbf{H_3A}]}$$

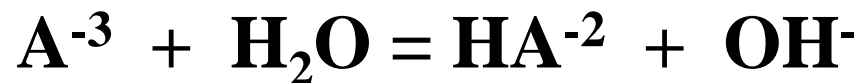


$$K_{a2} = \frac{[\mathbf{H^+}][\mathbf{HA^{-2}}]}{[\mathbf{H_2A^-}]}$$



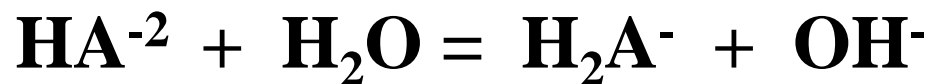
$$K_{a3} = \frac{[\mathbf{H^+}][\mathbf{A^{-3}}]}{[\mathbf{HA^{-2}}]}$$

Polyprotic Bases



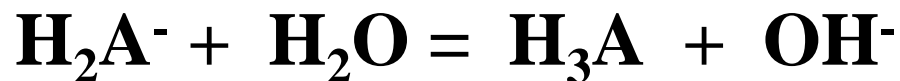
$$K_{b1} = \frac{[\text{OH}^{-}][\text{HA}^{-2}]}{[\text{A}^{-3}]}$$

$$K_{b1} = K_w/K_{a3}$$



$$K_{b2} = \frac{[\text{OH}^{-}][\text{H}_2\text{A}^{-2}]}{[\text{HA}^{-2}]}$$

$$K_{b2} = K_w/K_{a2}$$



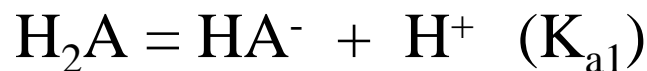
$$K_{b3} = \frac{[\text{OH}^{-}][\text{H}_3\text{A}]}{[\text{H}_2\text{A}^{-}]}$$

$$K_{b3} = K_w/K_{a1}$$

For most polyprotic acids, the K_a values are fairly different indicating that there must be fairly large pH changes (2 or more pH units) to dissociate the proton (H^+) from the molecule.

So for a diprotic acid (H_2A)...

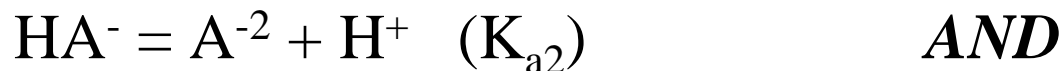
At **acidic** pH values ($pH < pK_{a1}$), mainly the acidic form of the molecule (H_2A) is present.



At **basic** pH values ($pH > pK_{a2}$), mainly the basic form of the molecule (A^{-2}) is present.

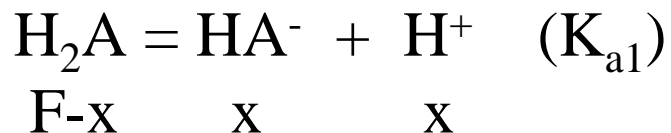


At **intermediate** pH values ($pK_{a1} < pH < pK_{a2}$), the intermediate form of the molecule (HA^-) is present.



How to calculate the concentrations of the different forms of a diprotic acid.

At **acidic** pH values ($\text{pH} < \text{pK}_{a1}$),



$$x^2 / (\text{F} - x) = \text{K}_{a1}$$

So.... $[\text{H}_2\text{A}] = \text{F} - x$

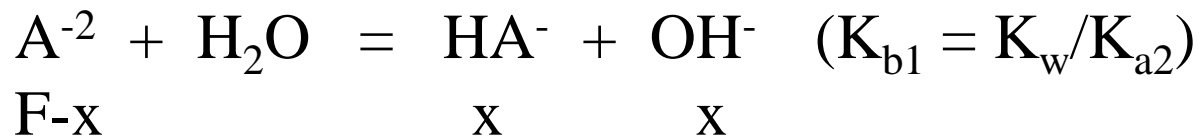
$$[\text{HA}^-] = x$$

$$[\text{H}^+] = x$$

To find A^{2-} , recall that A^{2-} is formed when HA^- loses H^+ :

$$\begin{aligned} \text{HA}^- &= \text{A}^{2-} + \text{H}^+ \quad (\text{K}_{a2}) \quad \text{so} \quad [\text{A}^{2-}] = \text{K}_{a2}[\text{HA}^-] / [\text{H}^+] \\ &= \text{K}_{a2} x / x = \text{K}_{a2} \end{aligned}$$

At **basic** pH values ($\text{pH} > \text{pK}_{\text{a}2}$),



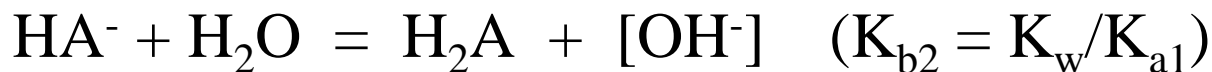
$$x^2 / (\text{F} - x) = \text{K}_{\text{b}1} = \text{K}_{\text{w}} / \text{K}_{\text{a}2}$$

So.... $[\text{A}^{-2}] = \text{F} - x$

$$[\text{HA}^{-}] = x$$

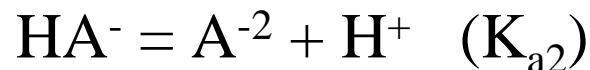
$$[\text{OH}^{-}] = x \text{ and } [\text{H}^{+}] = \text{K}_{\text{w}} / [\text{OH}^{-}] = \text{K}_{\text{w}} / x$$

To find H_2A , recall that H_2A is formed when HA^{-} gains H^{+} :



$$\text{So } [\text{H}_2\text{A}] = \text{K}_{\text{b}2} [\text{HA}^{-}] / [\text{OH}^{-}] = \text{K}_{\text{b}2} x / x = \text{K}_{\text{b}2}$$

At **intermediate** pH values ($pK_{a1} < pH < pK_{a2}$),



AND



If $[HA^-] \approx F$, then

$$K_{a2} = [A^{2-}] [H^+] / [HA^-] \quad \text{so} \quad [A^{2-}] = K_{a2} [HA^-] / [H^+]$$

$$\begin{aligned} K_{b2} &= [H_2A] [OH^-] / [HA^-] \quad \text{so} \quad [H_2A] = K_{b2} [HA^-] / [OH^-] \\ &= (K_w/K_{a1}) [HA^-] / (K_w/[H^+]) \\ &= [H^+] [HA^-] / K_{a1} \end{aligned}$$

$$[H^+] = \sqrt{K_{a1} K_{a2} F + K_{a1} K_w} / (K_{a1} + F) \quad (\text{see Harris pp. 207=208 for derivation of } [H^+] \text{ equation})$$

NOTE: $pH \approx \frac{1}{2} (pK_{a1} + pK_{a2})$

Polyprotic Acid



$$K_{a1} = \frac{[\text{H}^+][\text{H}_2\text{A}^-]}{[\text{H}_3\text{A}]}$$

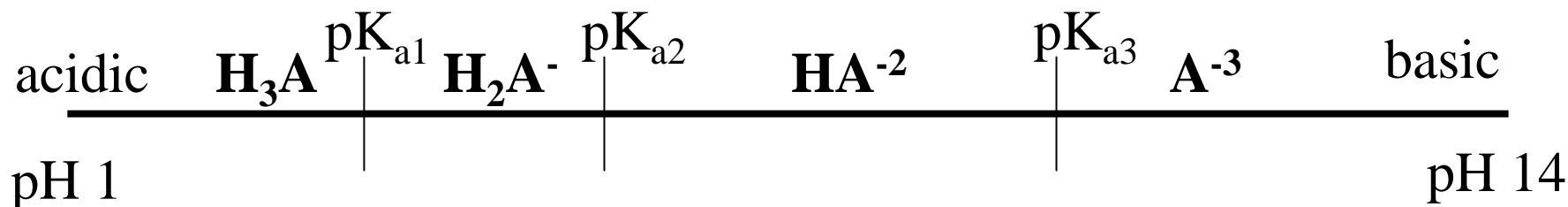


$$K_{a2} = \frac{[\text{H}^+][\text{HA}^{-2}]}{[\text{H}_2\text{A}^-]}$$



$$K_{a3} = \frac{[\text{H}^+][\text{A}^{-3}]}{[\text{HA}^{-2}]}$$

Dominant Species:



Find the pH and the concentrations of H_2SO_3 (sulfurous acid), HSO_3^- , and SO_3^{2-} in each solution ($\text{pK}_{\text{a}1} = 1.91$, $\text{pK}_{\text{a}2} = 7.18$):

a) 0.050 M H_2SO_3

b) 0.050 M NaHSO_3

c) 0.050 M Na_2SO_3