POLYPROTIC ACIDS AND BASES H Ch 10, Z Ch 7.7

To be reviewed when studying titrations

Polyprotic Acids and Bases, 10-1 and 10-3

polyprotic acid - capable of donating more than one proton
polyprotic base - capable of accepting more than one proton

recognize the acidity/basicity of some salt solutions: K_2CO_3, $NaHCO_3$, $CaHPO_4$, NH_4Cl, *etc.*

EX 1. How would one treat a solution of sulfuric acid where $K_a = 1.03 \times 10^{-2}$?

$$H_2SO_4(aq) + H_2O(l) \;<=>\; H_3O^+(aq) + HSO_4^-(aq)$$

$$HSO_4^-(aq) + H_2O(l) \;<=>\; H_3O^+(aq) + SO_4^{2-}(aq)$$

EX 2. What is the pH and concentration of **all** species present in a 5.00 M solution of phosphoric acid?

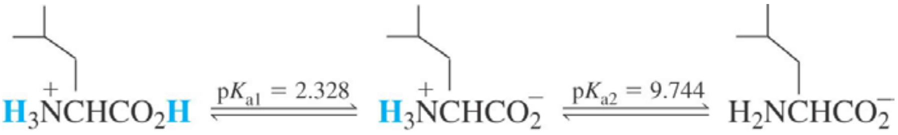
$K_{a1} = 7.11 \times 10^{-3}$ $H_3PO_4(aq) + H_2O(l) \;<=>\; H_3O^+(aq) + H_2PO_4^-(aq)$ $pK_{a1} = 2.1481$

$K_{a2} = 6.34 \times 10^{-8}$ $H_2PO_4^-(aq) + H_2O(l) \;<=>\; H_3O^+(aq) + HPO_4^{2-}(aq)$ $pK_{a2} = 7.1979$

$K_{a3} = 4.22 \times 10^{-13}$ $HPO_4^{2-}(aq) + H_2O(l) \;<=>\; H_3O^+(aq) + PO_4^{2-}(aq)$ $pK_{a3} = 12.3746$

EX 3. Using the phosphoric acid system in example 2 devise three different buffer systems. Give the pH range over which each buffer would be useful.

Diprotic Acid



$$H_3\overset{+}{N}CHCO_2H \xrightleftharpoons{pK_{a1} = 2.328} H_3\overset{+}{N}CHCO_2^- \xrightleftharpoons{pK_{a2} = 9.744} H_2NCHCO_2^-$$

EX 4. What is the pH of a 0.050 F aqueous solution of $NaHSO_3$? For sulfurous acid $K_{a1} = 1.39 \times 10^{-2}$, $K_{a2} = 6.73 \times 10^{-8}$

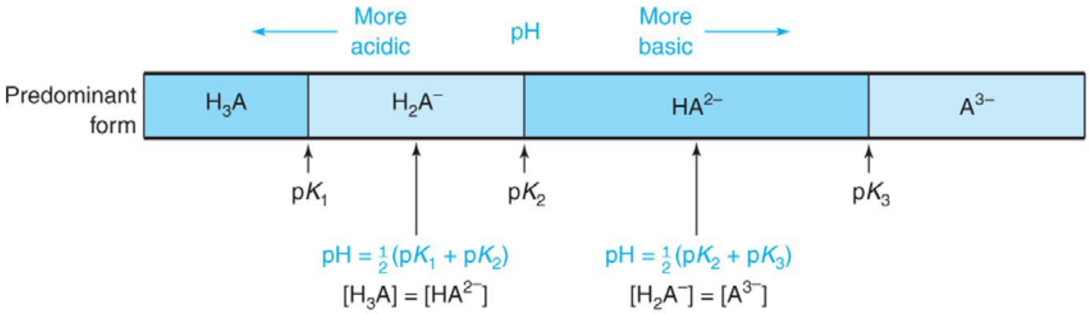
Polyprotic Buffers, 10-3

There is a different Henderson-Hasselbalch equation for conjugate acid/base pair of principal species. Consider the weak tripotic acid H_3A. Solutions buffered around three different pH's can be made from this system (using their salts).

$$\mathrm{pH} = \mathrm{pK_{a1}} + \log \frac{[H_2A^-]}{[H_3A]} \quad \text{and} \quad \mathrm{pH} = \mathrm{pK_{a2}} + \log \frac{[H_2A^-]}{[H_2A^-]} \quad \text{and} \quad \mathrm{pH} = \mathrm{pK_{a3}} + \log \frac{[H_2A^-]}{[HA^{2-}]}$$

Predominant Species, 10-4 - speciation

By comparing the pH with pK_a one can identify the principal species and estimate their concentration (a pH unit of 1 corresponds to a factor of 10 in concentration).

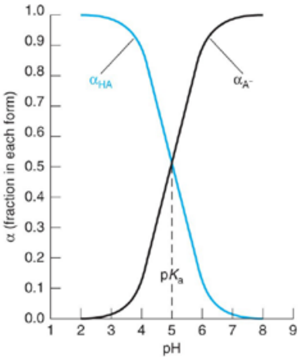


Fractional Composition Diagrams, 10-5

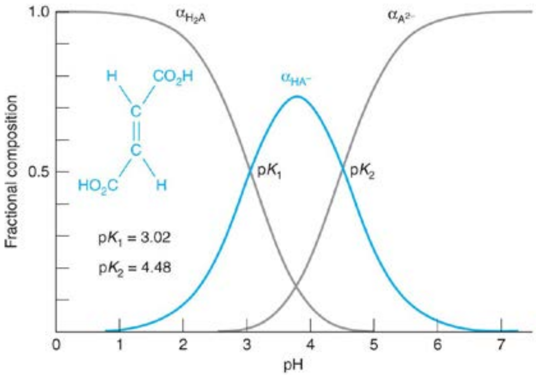
α versus pH

Fractional composition diagram of a monoprotic system with pK_a = 5.00. Below pH 5, HA is the dominant form, whereas, above pH 5, A^- dominates.

monoprotic



diprotic



How to Treat Polyprotic Acid-Base Equilibria, 10-3

1. treat strongest acid as a monoprotic acid - check
2. treat strongest base as a monobasic base - check
3. treat all others as an **intermediate form**

a) diprotic, H_2A

1) treat a solution of H_2A as monoprotic weak acid, $K_a = K_{a1} = K_1$

2) treat a solution of HA^- as intermediate form of diprotic acid, $K_{a1} = K_1$, $K_{a2} = K_2$

e.g., $LiHSO_3$

$$[H^+] = \sqrt{\frac{K_1K_2[HA] + K_1K_w}{K_1 + [HA]}} \approx \sqrt{\frac{K_1K_2F + K_1K_w}{K_1 + F}}$$

$LiHSO_4$ is not a diprotic acid intermediate form since HSO_4^- is the conjugate base of the strong acid, H_2SO_4. HSO_4^- only behaves as an acid as it is too weak of a base.

1) major species is generally $[HA^-]$ => replace $[HA^-]$ by F as done above

2) if $K_w \ll K_2 F$ and $K_1 \ll F$ then

$$[H^+] = \sqrt{K_1K_2} \qquad \text{or} \qquad \text{pH} \approx \frac{1}{2}(\text{p}K_1 + \text{p}K_2)$$

3) treat a solution of A^{2-} as monobasic weak base, $K_b = K_{b1} = K_w/K_{a2}$ *e.g.*, Li_2SO_3

b) extend to triprotic, H_3A

1) treat a solution of H_3A as monoprotic weak acid, $K_a = K_{a1} = K_1$

2) treat a solution of H_2A^- as intermediate form of diprotic acid, $K_{a1} = K_1$, $K_{a2} = K_2$

e.g., NaH_2PO_4

$$[H^+] \approx \sqrt{\frac{K_1K_2F + K_1K_w}{K_1 + F}}$$

3) treat a solution of HA^{2-} as intermediate form of diprotic acid, $K_{a2} = K_2$, $K_{a3} = K_3$

e.g., Na_2HPO_4

$$[H^+] \approx \sqrt{\frac{K_2K_3F + K_2K_w}{K_2 + F}}$$

4) treat a solution of A^{3-} as monobasic weak base, $K_b = K_{b1} = K_w/K_{a3}$

4. salt solutions can be acidic or basic and need to be treated accordingly