Buffer Solutions

- A buffer solution is comprised of a mixture of an acid (base) with its conjugate base (acid) that resists changes in pH when additional acid or base is added

- The Henderson-Hasselbalch Equation describes the pH in buffer solutions:

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

Henderson-Hasselbalch Equation:

[A⁻] = concentration of conjugate base

[HA] = concentration of acid

Buffer Solutions

- Example: Find the pH of a solution with [CH₃COOH] = 0.250 M and [NaCH₃COO] = 0.315 M

    [HA] = 0.250 M

    [A⁻] = 0.315 M

    $K_a = 1.8 \times 10^{-5} \Rightarrow pK_a = -\log(1.8 \times 10^{-5}) = 4.7$

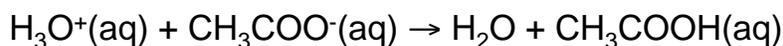$$pH = pK_a + \log\frac{[A^-]}{[HA]} = 4.7 + \log\left(\frac{0.315}{0.250}\right) = 4.8$$

Buffer Solutions

- Example: If we now add 10.0 mL of 0.100 M HCl to 50.0 mL of the buffer solution, determine the new pH of the solution.

HCl, a strong acid, reacts with the acetate ion base to form water and acetic acid:

$$H_3O^+(aq) + CH_3COO^-(aq) \rightarrow H_2O + CH_3COOH(aq)$$

- We must first account for the dilution factors ($C_1V_1=C_2V_2$):

$[H_3O^+]$ = (.100 M)(10.0 mL)/(60.0 mL) = 0.0167 M

$[CH_3COO^-]$ = (.315 M)(50.0 mL)/(60.0 mL) = 0.263 M

$[CH_3COOH]$ = (.250 M)(50.0 mL)/(60.0 mL) = 0.208 M

Buffer Solutions

- Example (con't.):
  - Now allow reaction between HCl and acetate to occur—since HCl is a strong acid, it will react completely as long as base remains in solution:

$$H_3O^+(aq) + CH_3COO^-(aq) \rightarrow H_2O + CH_3COOH(aq)$$
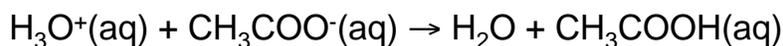
.0167 − .0167   .263 − .0167   .208 + .0167

$[CH_3COOH]$ = .208 + .0167 = .225 M

$[CH_3COO^-]$ = .263 - .0167 = .246 M

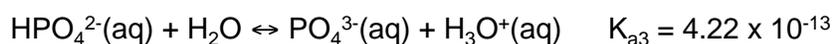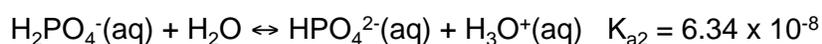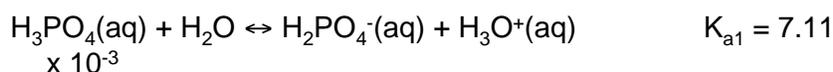$$pH = pK_a + \log\frac{[A^-]}{[HA]} = 4.7 + \log\left(\frac{0.246}{0.225}\right) = 4.7$$

> If the same amount of acid had been added to pure water, the pH would change from 7.0 to 1.8
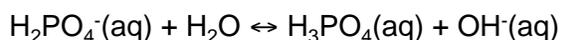
Polyprotic Acids and Bases

- If an acid can donate more than one hydrogen ion, then it is called a diprotic (2 H^+ ions) or triprotic (3 H^+ ions) acid

- If a base can accept more than one hydrogen atom, it is called a diprotic (2 H^+ ions) or triprotic (3 H^+ ions) base
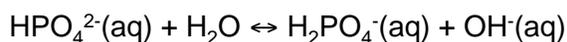
- Example: H_3PO_4

$H_3PO_4(aq) + H_2O \leftrightarrow H_2PO_4^-(aq) + H_3O^+(aq)$ $\quad\quad K_{a1} = 7.11 \times 10^{-3}$

$H_2PO_4^-(aq) + H_2O \leftrightarrow HPO_4^{2-}(aq) + H_3O^+(aq)$ $\quad K_{a2} = 6.34 \times 10^{-8}$

$HPO_4^{2-}(aq) + H_2O \leftrightarrow PO_4^{3-}(aq) + H_3O^+(aq)$ $\quad K_{a3} = 4.22 \times 10^{-13}$

Polyprotic Acids and Bases

- The resulting conjugate bases also can be polyprotic:

$H_2PO_4^-(aq) + H_2O \leftrightarrow H_3PO_4(aq) + OH^-(aq)$

$\quad K_{a1} \cdot K_{b1} = K_w$ $\quad\quad\quad K_{b1} = 1.41 \times 10^{-12}$

$HPO_4^{2-}(aq) + H_2O \leftrightarrow H_2PO_4^-(aq) + OH^-(aq)$

$\quad K_{a2} \cdot K_{b2} = K_w$ $\quad\quad\quad K_{b2} = 1.58 \times 10^{-7}$

$PO_4^{3-}(aq) + H_2O \leftrightarrow HPO_4^{2-}(aq) + OH^-(aq)$

$\quad K_{a3} \cdot K_{b3} = K_w$ $\quad\quad\quad K_{b3} = 2.37 \times 10^{-2}$

- Species that can both accept and donate a hydrogen ion are called *amphiprotic*

Polyprotic Acids and Bases

- Suppose we dissolve NaH_2PO_4 in water to produce a solution that is 0.100 M NaH_2PO_4. The resulting $H_2PO_4^-$(aq) can behave either as an acid or a base. Which process will dominate and what will be the resulting pH?

Acid: $H_2PO_4^-$(aq) + H_2O ↔ HPO_4^{2-}(aq) + H_3O^+(aq)

Base: $H_2PO_4^-$(aq) + H_2O ↔ H_3PO_4 (aq) + OH^-(aq)
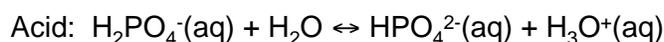
- We can use the requirements of charge and mass balance for chemical reactions to determine a solution to this problem (see section 8-4)

Polyprotic Acids and Bases

- Find the pH of a 0.100 M NaH_2PO_4 solution:
- Charge balance—the sum total of positive charges must equal the sum total of negative charges
    - Positively charged species are H_3O^+ and Na^+
    - Negatively charged species are $H_2PO_4^-$, HPO_4^{2-}, and OH^-

$[H_3O^+] + [Na^+] = [H_2PO_4^-] + 2[HPO_4^{2-}] + [OH^-]$

    - We use $2[HPO_4^{2-}]$ because this ion has a -2 charge, so we need two singly charged cations to balance the negative charge from this anion

Polyprotic Acids and Bases

- Find the pH of a 0.100 M NaH_2PO_4 solution:

- Mass balance—the concentrations of all species containing PO_4^{3-} must equal the formal concentration (F) of the initial amount prepared in the solution:

$F = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}]$

In this particular example, $[Na^+] = F$

Polyprotic Acids and Bases

- Find the pH of a 0.100 M NaH_2PO_4 solution:

substitution of mass balance relationship into charge balance expression:

$$[H_3O^+] + [Na^+] = [H_2PO_4^-] + 2[HPO_4^{2-}] + [OH^-]$$

$$[Na^+] = F = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}]$$

$$[H_3O^+] + [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}]$$

$$= [H_2PO_4^-] + 2[HPO_4^{2-}] + [OH^-]$$

$$[H_3O^+] + [H_3PO_4] - [HPO_4^{2-}] - [OH^-] = 0$$

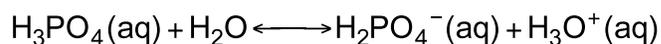# Polyprotic Acids and Bases

- Find the pH of a 0.100 M NaH_2PO_4 solution:

$[H_3O^+] + [H_3PO_4] - [HPO_4^{2-}] - [OH^-] = 0$

Using the two acid dissociation reactions:

$$H_3PO_4(aq) + H_2O \longleftrightarrow H_2PO_4^-(aq) + H_3O^+(aq)$$

$$K_{a1} = \frac{[H_2PO_4^-][H_3O^+]}{[H_3PO_4]} \Rightarrow [H_3PO_4] = \frac{[H_2PO_4^-][H_3O^+]}{K_{a1}}$$

$$H_2PO_4^-(aq) + H_2O \longleftrightarrow HPO_4^{2-}(aq) + H_3O^+(aq)$$
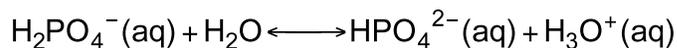
$$K_{a2} = \frac{[HPO_4^{2-}][H_3O^+]}{[H_2PO_4^-]} \Rightarrow [HPO_4^{2-}] = \frac{K_{a2}[H_2PO_4^-]}{[H_3O^+]}$$

Polyprotic Acids and Bases

- Find the pH of a 0.100 M NaH_2PO_4 solution:

$$[H_3O^+] + \frac{[H_2PO_4^-][H_3O^+]}{K_{a1}} - \frac{K_{a2}[H_2PO_4^-]}{[H_3O^+]} - \frac{K_w}{[H_3O^+]} = 0$$

$$[H_3O^+]^2\left(1 + \frac{[H_2PO_4^-]}{K_{a1}}\right) = K_{a2}[H_2PO_4^-] + K_w$$

$$[H_3O^+]^2 = \left\{\frac{K_{a1}(K_{a2}[H_2PO_4^-] + K_w)}{K_{a1} + [H_2PO_4^-]}\right\} \qquad (eqn\ 10 - 10)$$

Polyprotic Acids and Bases

- Find the pH of a 0.100 M NaH_2PO_4 solution:

In order to solve this, we need the equilibrium concentration of $[H_2PO_4^-]$

Since $H_2PO_4^-$ is both a weak acid and a weak base, we don't expect either reaction to proceed to a great extent, so $[H_2PO_4^-] \approx F$

$$[H_3O^+] \approx \left\{ \frac{K_{a1}(K_{a2}F + K_w)}{K_{a1} + F} \right\}^{1/2}$$

Polyprotic Acids and Bases

- Find the pH of a 0.100 M NaH_2PO_4 solution:

$K_{a1} = 7.11 \times 10^{-3}$

$K_{a2} = 6.34 \times 10^{-8}$

$F = 0.100$ M

$$[H_3O^+] = \left\{ \frac{(7.11x10^{-3})[(6.34x10^{-8})(0.100) + (1.00x10^{-14})]}{7.11x10^{-3} + 0.100} \right\}^{1/2}$$

$$= 2.05x10^{-5}$$

$$pH = 4.69$$

Titration of a Weak Base with a Strong Acid

- Remember that a strong acid is one in which dissociation to H_3O^+ and A^- is complete
- The titration reaction prior to the equivalence point is:

$H_3O^+(aq) + B(aq) \rightarrow HB^+(aq) + H_2O$

- Since the acid is strong, all H_3O^+ from the acid reacts with B; the dissociation of HB^+ back to reactants determines the pH of the solution

Titration of a Weak Base with a Strong Acid

Before titration begins

$B + H_2O \leftrightarrow HB^+ + OH^-$ $K_b = [HB^+][OH^-]/[B]$

F-x   x   x
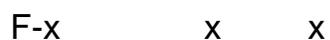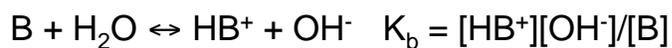
$K_b = x^2/(F-x)$

$[H_3O^+] = K_w/[OH^-] = K_w/x$

Titration of a Weak Base with a Strong Acid

Titration before the equivalence point
Initial conditions:

   $[B]_o$ = initial concentration of base

   V_b = initial volume of base

   $[HA]$ = concentration of strong acid

   V_a = volume of acid added

   $V_{tot} = V_a + V_b$

Titration of a Weak Base with a Strong Acid

If we know the ratio of $[B]$ to $[HB^+]$, we can determine the pH using the Henderson-Hasselbalch equation:

   $HA + B \rightarrow HB^+(aq) + A^-(aq)$

Let x equal moles of HA added: $x = [HA]V_a$

Then, $[B] = ([B]_o V_b - x)/V_{tot}$ and $[HB^+] = x/V_{tot}$

$$pH = pK_a + \log\left\{\frac{([B]_o V_b - x)/V_{tot}}{x/V_{tot}}\right\}$$

$$= pK_a + \log\left\{\frac{[B]_o V_b - x}{x}\right\}$$

Titration of a Weak Base with a Strong Acid

At equivalence point

Addition of strong acid has converted all base to its conjugate acid HB$^+$

This dissociates back to for B and H$_3$O$^+$

$HB^+ + H_2O \leftrightarrow B + H_3O^+$ $Ka = K_w/K_b = [B][H_3O^+]/[HB^+]$

Titration of a Weak Base with a Strong Acid

After the equivalence point

Once the base has all reacted with strong acid, the only thing remaining in solution the weak conjugate acid, HB$^+$, and hydronium from the excess strong acid added

pH is determined solely from the added excess strong acid, taking into account the dilution of acid in solution
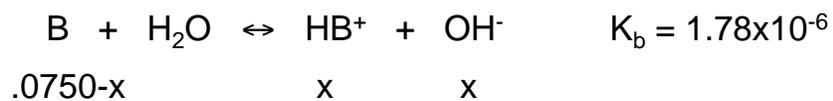
$[H_3O^+] = [HA](V_{a,xs} - V_{a,eq\ pt})/V_{tot}$

Titration of a Weak Base with a Strong Acid

Example: let $[HA] = 0.1000$ M, $[B]_o = 0.0750$ M, $V_b = 25.00$ mL, $pK_b = 5.75 \Rightarrow pK_a = 8.25$

Before titration begins:

$$B + H_2O \leftrightarrow HB^+ + OH^- \qquad K_b = 1.78 \times 10^{-6}$$

.0750-x   x   x

$x^2 = (1.78 \times 10^{-6})(.0750-x)$

$[OH^-] = 3.66 \times 10^{-4}$ M

pH = 10.56

Titration of a Weak Base with a Strong Acid

Titration of weak base, B, with strong acid, HA
$[B]_o = 0.0750$ M $V_b = 25.00$ mL
$[HA] = 0.1000$ M $pK_b = 5.75$

equivalence point

Volume HA added (mL)