

## 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:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Henderson-Hasselbalch Equation:  
 [A<sup>-</sup>] = concentration of conjugate base  
 [HA] = concentration of acid

## Buffer Solutions

- Example: Find the pH of a solution with [CH<sub>3</sub>COOH] = 0.250 M and [NaCH<sub>3</sub>COO] = 0.315 M
 
$$[\text{HA}] = 0.250 \text{ M}$$

$$[\text{A}^-] = 0.315 \text{ M}$$

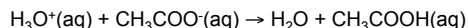
$$K_a = 1.8 \times 10^{-5} \Rightarrow \text{p}K_a = -\log(1.8 \times 10^{-5}) = 4.7$$

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

## 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:



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

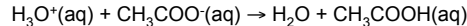
$$[\text{H}_3\text{O}^+] = (0.100 \text{ M})(10.0 \text{ mL}) / (60.0 \text{ mL}) = 0.0167 \text{ M}$$

$$[\text{CH}_3\text{COO}^-] = (0.315 \text{ M})(50.0 \text{ mL}) / (60.0 \text{ mL}) = 0.263 \text{ M}$$

$$[\text{CH}_3\text{COOH}] = (0.250 \text{ M})(50.0 \text{ mL}) / (60.0 \text{ mL}) = 0.208 \text{ M}$$

## 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:



$$.0167 - .0167 \quad .263 - .0167 \quad .208 + .0167$$

$$[\text{CH}_3\text{COOH}] = .208 + .0167 = .225 \text{ M}$$

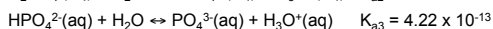
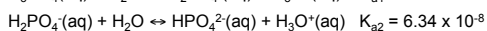
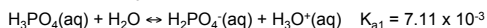
$$[\text{CH}_3\text{COO}^-] = .263 - .0167 = .246 \text{ M}$$

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

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<sup>+</sup> ions) or triprotic (3 H<sup>+</sup> ions) acid
- If a base can accept more than one hydrogen atom, it is called a diprotic (2 H<sup>+</sup> ions) or triprotic (3 H<sup>+</sup> ions) base
- Example: H<sub>3</sub>PO<sub>4</sub>



## Polyprotic Acids and Bases

- The resulting conjugate bases also can be polyprotic:
 
$$\text{H}_2\text{PO}_4^-(\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{PO}_4(\text{aq}) + \text{OH}^-(\text{aq})$$

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

$$\text{HPO}_4^{2-}(\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{PO}_4^-(\text{aq}) + \text{OH}^-(\text{aq})$$

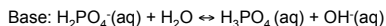
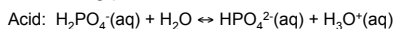
$$K_{a2} \cdot K_{b2} = K_w \quad K_{b2} = 1.58 \times 10^{-7}$$

$$\text{PO}_4^{3-}(\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{HPO}_4^{2-}(\text{aq}) + \text{OH}^-(\text{aq})$$

$$K_{a3} \cdot K_{b3} = K_w \quad K_{b3} = 2.37 \times 10^{-2}$$
- Species that can both accept and donate a hydrogen ion are called *amphiprotic*

## Polyprotic Acids and Bases

- Suppose we dissolve  $\text{NaH}_2\text{PO}_4$  in water to produce a solution that is 0.100 M  $\text{NaH}_2\text{PO}_4$ . The resulting  $\text{H}_2\text{PO}_4^-(\text{aq})$  can behave either as an acid or a base. Which process will dominate and what will be the resulting pH?



- We can use the requirements of charge and mass balance for chemical reactions to determine a solution to this problem (see section 8-4 or 7-4)

## Polyprotic Acids and Bases

- Find the pH of a 0.100 M  $\text{NaH}_2\text{PO}_4$  solution:
- Charge balance—the sum total of positive charges must equal the sum total of negative charges
  - Positively charged species are  $\text{H}_3\text{O}^+$  and  $\text{Na}^+$
  - Negatively charged species are  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ , and  $\text{OH}^-$
$$[\text{H}_3\text{O}^+] + [\text{Na}^+] = [\text{H}_2\text{PO}_4^-] + 2[\text{HPO}_4^{2-}] + [\text{OH}^-]$$
  - We use  $2[\text{HPO}_4^{2-}]$  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  $\text{NaH}_2\text{PO}_4$  solution:
- Mass balance—the concentrations of all species containing  $\text{PO}_4^{3-}$  must equal the formal concentration (F) of the initial amount prepared in the solution:

$$F = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}]$$

In this particular example,  $[\text{Na}^+] = F$

## Polyprotic Acids and Bases

- Find the pH of a 0.100 M  $\text{NaH}_2\text{PO}_4$  solution:
- substitution of mass balance relationship into charge balance expression:

$$[\text{H}_3\text{O}^+] + [\text{Na}^+] = [\text{H}_2\text{PO}_4^-] + 2[\text{HPO}_4^{2-}] + [\text{OH}^-]$$

$$[\text{Na}^+] = F = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}]$$

$$[\text{H}_3\text{O}^+] + [\text{H}_3\text{PO}_4] + \cancel{[\text{H}_2\text{PO}_4^-]} + \cancel{[\text{HPO}_4^{2-}]} = \cancel{[\text{H}_2\text{PO}_4^-]} + 2[\text{HPO}_4^{2-}] + [\text{OH}^-]$$

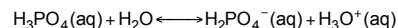
$$[\text{H}_3\text{O}^+] + [\text{H}_3\text{PO}_4] - [\text{HPO}_4^{2-}] - [\text{OH}^-] = 0$$

## Polyprotic Acids and Bases

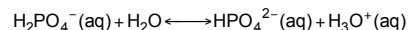
- Find the pH of a 0.100 M  $\text{NaH}_2\text{PO}_4$  solution:

$$[\text{H}_3\text{O}^+] + [\text{H}_3\text{PO}_4] - [\text{HPO}_4^{2-}] - [\text{OH}^-] = 0$$

Using the two acid dissociation reactions:



$$K_{a1} = \frac{[\text{H}_2\text{PO}_4^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{PO}_4]} \Rightarrow [\text{H}_3\text{PO}_4] = \frac{[\text{H}_2\text{PO}_4^-][\text{H}_3\text{O}^+]}{K_{a1}}$$



$$K_{a2} = \frac{[\text{HPO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]} \Rightarrow [\text{HPO}_4^{2-}] = \frac{K_{a2}[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{O}^+]}$$

## Polyprotic Acids and Bases

- Find the pH of a 0.100 M  $\text{NaH}_2\text{PO}_4$  solution:

$$[\text{H}_3\text{O}^+] + \frac{[\text{H}_2\text{PO}_4^-][\text{H}_3\text{O}^+]}{K_{a1}} - \frac{K_{a2}[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{O}^+]} - \frac{K_w}{[\text{H}_3\text{O}^+]} = 0$$

$$[\text{H}_3\text{O}^+]^2 \left( 1 + \frac{[\text{H}_2\text{PO}_4^-]}{K_{a1}} \right) = K_{a2}[\text{H}_2\text{PO}_4^-] + K_w$$

$$[\text{H}_3\text{O}^+]^2 = \left\{ \frac{K_{a1}(K_{a2}[\text{H}_2\text{PO}_4^-] + K_w)}{K_{a1} + [\text{H}_2\text{PO}_4^-]} \right\} \quad (\text{eqn 10 - 10 or 9 - 10})$$

## Polyprotic Acids and Bases

- Find the pH of a 0.100 M  $\text{NaH}_2\text{PO}_4$  solution:

In order to solve this, we need the equilibrium concentration of  $[\text{H}_2\text{PO}_4^-]$

Since  $\text{H}_2\text{PO}_4^-$  is both a weak acid and a weak base, we don't expect either reaction to proceed to a great extent, so  $[\text{H}_2\text{PO}_4^-] \approx F$

$$[\text{H}_3\text{O}^+] = \left\{ \frac{K_{a1}(K_{a2}F + K_w)}{K_{a1} + F} \right\}^{1/2}$$

## Polyprotic Acids and Bases

- Find the pH of a 0.100 M  $\text{NaH}_2\text{PO}_4$  solution:

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

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

$$F = 0.100 \text{ M}$$

$$[\text{H}_3\text{O}^+] = \left\{ \frac{(7.11 \times 10^{-3})[(6.34 \times 10^{-8})(0.100) + (1.00 \times 10^{-14})]}{7.11 \times 10^{-3} + 0.100} \right\}^{1/2}$$

$$= 2.05 \times 10^{-5}$$

$$\text{pH} = 4.69$$

## Titration of a Weak Base with a Strong Acid

- Remember that a strong acid is one in which dissociation to  $\text{H}_3\text{O}^+$  and  $\text{A}^-$  is complete
- The titration reaction prior to the equivalence point is:  
 $\text{H}_3\text{O}^+(\text{aq}) + \text{B}(\text{aq}) \rightarrow \text{HB}^+(\text{aq}) + \text{H}_2\text{O}$
- Since the acid is strong, all  $\text{H}_3\text{O}^+$  from the acid reacts with B; the dissociation of  $\text{HB}^+$  back to reactants determines the pH of the solution

## Titration of a Weak Base with a Strong Acid

Before titration begins



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

$$[\text{H}_3\text{O}^+] = K_w/[\text{OH}^-] = K_w/x$$

## Titration of a Weak Base with a Strong Acid

Titration before the equivalence point

Initial conditions:

$[\text{B}]_0$  = initial concentration of base

$V_b$  = initial volume of base

$[\text{HA}]$  = concentration of strong acid

$V_a$  = volume of acid added

$V_{\text{tot}} = V_a + V_b$

## Titration of a Weak Base with a Strong Acid

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



Let  $x$  equal moles of HA added:  $x = [\text{HA}]V_a$

Then,  $[\text{B}] = ([\text{B}]_0 V_b - x)/V_{\text{tot}}$  and  $[\text{HB}^+] = x/V_{\text{tot}}$

$$\text{pH} = \text{p}K_a + \log \left\{ \frac{([\text{B}]_0 V_b - x)/V_{\text{tot}}}{x/V_{\text{tot}}} \right\}$$

$$= \text{p}K_a + \log \left\{ \frac{[\text{B}]_0 V_b - x}{x} \right\}$$

### Titration of a Weak Base with a Strong Acid

#### At equivalence point

Addition of strong acid has converted all base to its conjugate acid  $\text{HB}^+$

This dissociates back to for B and  $\text{H}_3\text{O}^+$



### 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,  $\text{HB}^+$ , and hydronium from the excess strong acid added

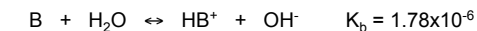
pH is determined solely from the added excess strong acid, taking into account the dilution of acid in solution

$$[\text{H}_3\text{O}^+] = [\text{HA}](V_{a,xs} - V_{a,eq pt})/V_{tot}$$

### Titration of a Weak Base with a Strong Acid

Example: let  $[\text{HA}] = 0.1000 \text{ M}$ ,  $[\text{B}]_0 = 0.0750 \text{ M}$ ,  $V_b = 25.00 \text{ mL}$ ,  $\text{p}K_b = 5.75 \Rightarrow \text{p}K_a = 8.25$

Before titration begins:



$$.0750 - x \quad \quad \quad x \quad \quad \quad x$$

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

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

$$\text{pH} = 10.56$$

### Titration of a Weak Base with a Strong Acid

