

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⁻] = concentration of conjugate base
 [HA] = concentration of acid

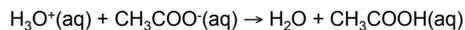
Buffer Solutions

- Example: Find the pH of a solution with [CH₃COOH] = 0.250 M and [NaCH₃COO] = 0.315 M
- $$[\text{HA}] = 0.250 \text{ M}$$
- $$[\text{A}^-] = 0.315 \text{ M}$$
- $$K_a = 1.8 \times 10^{-5} \Rightarrow \text{p}K_a = -\log(1.8 \times 10^{-5}) = 4.7$$
- $$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} = 4.7 + \log \left(\frac{0.315}{0.250} \right) = 4.8$$

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.

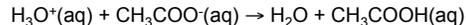
HCl, a strong acid, reacts with the acetate ion base to form water and acetic acid:



- We must first account for the dilution factors ($C_1V_1 = C_2V_2$):
- $$[\text{H}_3\text{O}^+] = (.100 \text{ M})(10.0 \text{ mL})/(60.0 \text{ mL}) = 0.0167 \text{ M}$$
- $$[\text{CH}_3\text{COO}^-] = (.315 \text{ M})(50.0 \text{ mL})/(60.0 \text{ mL}) = 0.263 \text{ M}$$
- $$[\text{CH}_3\text{COOH}] = (.250 \text{ M})(50.0 \text{ mL})/(60.0 \text{ mL}) = 0.208 \text{ M}$$

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:



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

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

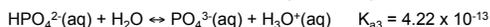
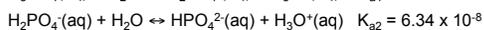
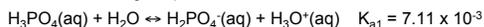
$$[\text{CH}_3\text{COO}^-] = .263 - .0167 = .246 \text{ M}$$

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

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⁺ 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: H₃PO₄

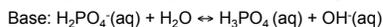
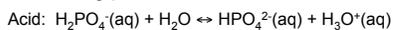


Polyprotic Acids and Bases

- 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 NaH_2PO_4 in water to produce a solution that is 0.100 M NaH_2PO_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)

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

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

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

Polyprotic Acids and Bases

- Find the pH of a 0.100 M NaH_2PO_4 solution: substitution of mass balance relationship into charge balance expression:

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

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

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

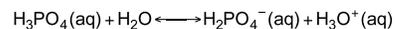
$$[\text{H}_3\text{O}^+] + [\text{H}_3\text{PO}_4] - [\text{HPO}_4^{2-}] - [\text{OH}^-] = 0$$

Polyprotic Acids and Bases

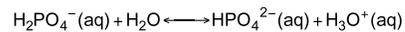
- Find the pH of a 0.100 M NaH_2PO_4 solution:

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

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 NaH_2PO_4 solution:

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

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

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

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 $[\text{H}_2\text{PO}_4^-]$
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 $[\text{H}_2\text{PO}_4^-] \approx F$

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

Polyprotic Acids and Bases

- Find the pH of a 0.100 M NaH_2PO_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 H_3O^+ and 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 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



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

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

Titration of a Weak Base with a Strong Acid

Titration before the equivalence point

Initial conditions:

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

$$V_b = \text{initial volume of base}$$

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

$$V_a = \text{volume of acid added}$$

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

Titration of a Weak Base with a Strong Acid

If we know the ratio of [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 HB^+

This dissociates back to form B and H_3O^+



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 is 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

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

Titration of a Weak Base with a Strong Acid

Example: let $[\text{HA}] = 0.1000 \text{ M}$, $[\text{B}]_0 = 0.0750 \text{ M}$, $V_0 = 25.00 \text{ mL}$, $\text{p}K_b = 5.75 \Rightarrow \text{p}K_a = 8.25$

Before titration begins:



$$.0750 - x \qquad \qquad x \qquad \qquad x$$

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

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

$$\text{pH} = 10.56$$

Titration of a Weak Base with a Strong Acid

