

Chapter 9 in the 9th Edition
Chapter 8 in the 8th Edition

Monoprotic Acid-Base Equilibria

Overview

- 9-1 Strong Acids and Bases
- 9-2 Weak Acids and Bases
- 9-3 Weak-Acid Equilibria
- 9-4 Weak-Base Equilibria
- 9-5 Buffers

9-1: Strong Acids and Bases

Calculating pH:

For practical concentrations ($\geq 10^{-6}$ M), pH or pOH is obtained directly from the formal concentration of acid or base.

What is the pH of a 1.5×10^{-3} M HCl solution?



$$\text{pH} = -\text{Log}(1.5 \times 10^{-3} \text{ M}), \quad \text{pH} = 2.82_4$$

$$2.82_4 + \text{pOH} = 14.00$$

$$\text{pOH} = 14.00 - 2.82_4$$

$$\text{pOH} = 11.18$$

$$\text{pH} + \text{pOH} = -\log K_w = 14.00 \text{ at } 25^\circ\text{C}$$

9-1: Strong Acids and Bases

EXAMPLE Activity Coefficient in a Strong-Acid Calculation

Calculate the pH of 0.10 M HBr, using activity coefficients.

Solution The ionic strength of 0.10 M HBr is $\mu = 0.10$ M, at which the activity coefficient of H^+ is 0.83 (Table 8-1). Remember that pH is $-\log \mathcal{A}_{\text{H}^+}$, not $-\log[\text{H}^+]$:

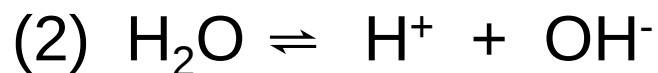
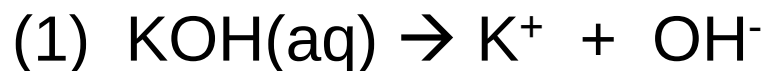
$$\text{pH} = -\log[\text{H}^+] \gamma_{\text{H}^+} = -\log(0.10)(0.83) = 1.08$$

TEST YOURSELF Calculate the pH of 0.010 M HBr in 0.090 M KBr. (*Answer:* 2.08)

9-1: Strong Acids and Bases

What is the pH of a 1.0×10^{-8} M KOH solution?

- Answer: It cannot be pH 6.00. It should be a basic solution with a pH higher than 7.00!
- There are two reactions that are important:



Use the systematic treatment of equilibrium.

9-1: Strong Acids and Bases

Equilibrium calculations:

- Write all pertinent equilibrium reactions
- Predict
- Set up equations
- Simplify (assumptions)
- Solve!

9-1: Strong Acids and Bases

What is the pH of a 1.0×10^{-8} M KOH solution?

- Write the equations:



- We have one equation and three unknowns: K^+ , OH^- , H^+ .
- We need two more equations. Write the **mass balance** (MB) and **charge balance** (CB):

$$\text{MB: } [\text{K}^+] = 1.0 \times 10^{-8} \text{ M}$$

$$\text{CB: } [\text{K}^+] + [\text{H}^+] = [\text{OH}^-]$$

9-1: Strong Acids and Bases

What is the pH of a 1.0×10^{-8} M KOH solution?

- Solve starting with the CB: $[H^+] = [OH^-] - [K^+]$
 $[H^+] = K_w/[H^+] - [K^+]$ substitute for $[OH^-]$
 $[H^+]^2 = K_w - [K^+] [H^+]$ multiply by $[H^+]$
 $[H^+]^2 + [K^+] [H^+] - K_w = 0$ rearrange
 $[H^+]^2 + 1.0 \times 10^{-8} [H^+] - K_w = 0$ $[K^+] = 1.0 \times 10^{-8}$ M, solve for $[H^+]$
 $[H^+] = 9.5 \times 10^{-8}$ M; pH = 7.02

- The Quadratic Formula**, used to find the value of x in the equation **$ax^2 + bx + c = 0$**

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

9-1: Strong Acids and Bases

What is the pH of a 1.0×10^{-7} M HBr solution?

- Write the equations:



- We have one equation and three unknowns: Br^- , OH^- , H^+ .
- We need two more equations. Write the **mass balance** (MB) and **charge balance** (CB):

$$\text{MB: } [\text{Br}^-] = 1.0 \times 10^{-7} \text{ M}$$

$$\text{CB: } [\text{H}^+] = [\text{OH}^-] + [\text{Br}^-]$$

9-1: Strong Acids and Bases

What is the pH of a 1.0×10^{-7} M HBr solution?

- Solve starting with the CB: $[H^+] = [OH^-] + [Br^-]$
 $[H^+] = K_w/[H^+] + [Br^-]$ substitute for $[OH^-]$
 $[H^+]^2 = K_w + [Br^-] [H^+]$ multiply by $[H^+]$
 $[H^+]^2 - [Br^-] [H^+] - K_w = 0$ rearrange
 $[H^+]^2 - 1.0 \times 10^{-7} [H^+] - K_w = 0$ $[Br^-] = 1.0 \times 10^{-7}$ M, solve for $[H^+]$
 $[H^+] = 1.62 \times 10^{-7}$ M; pH = 6.79

- The Quadratic Formula**, used to find the value of x in the equation **$ax^2 + bx + c = 0$**

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

9-1: Strong Acids and Bases

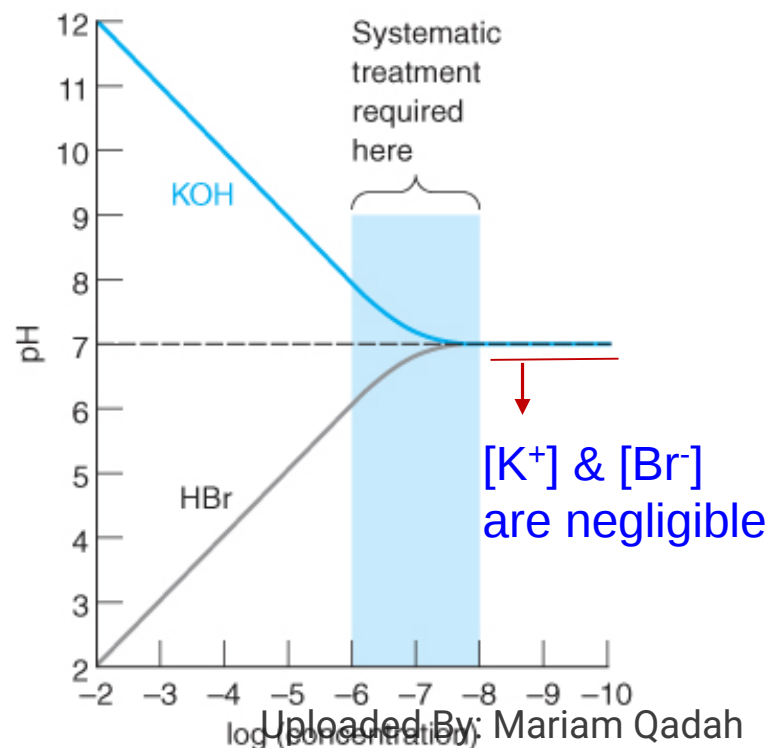
Calculating pH:

- When the concentration is near 10^{-7} M, we use the systematic treatment of equilibrium to calculate pH.
- At still lower concentrations, the pH is 7.00, set by autoprotolysis of the solvent.

$$[\text{H}^+] = [\text{OH}^-] - [\text{K}^+] \text{ or}$$

$$[\text{H}^+] = [\text{OH}^-] + [\text{Br}^-]$$

at lower $[\text{K}^+]$ or $[\text{Br}^-]$ ($< 10^{-8}$ M), $[\text{H}^+] \approx [\text{OH}^-]$



9-2:Weak Acids and Bases

Calculating the pH of weak acids:

- For the reaction $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$, we set up and solve the equation

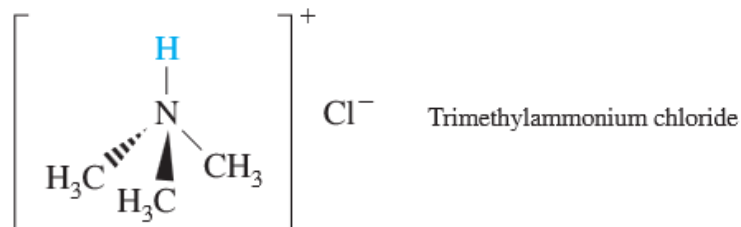
$$\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{x^2}{F - x} = K_a$$

- where $[\text{H}^+] = [\text{A}^-] = x$, and $[\text{HA}] = F - x$.

9-2: Weak Acids and Bases

EXAMPLE A Weak-Acid Problem

Find the pH of 0.050 M trimethylammonium chloride. $\text{p}K_a = 9.799$, $K_a = 10^{-9.799} = 1.59 \times 10^{-10}$



Solution We assume that ammonium halide salts are completely dissociated to give $(\text{CH}_3)_3\text{NH}^+$ and Cl^- . We then recognize that trimethylammonium ion is a weak acid, being the conjugate acid of trimethylamine, $(\text{CH}_3)_3\text{N}$, a weak base. Cl^- has no basic or acidic properties and should be ignored. In Appendix G, we find trimethylammonium ion listed as trimethylamine but drawn as trimethylammonium ion, with $\text{p}K_a = 9.799$ at an ionic strength of $\mu = 0$. So,

$$K_a = 10^{-\text{p}K_a} = 10^{-9.799} = 1.59 \times 10^{-10}$$

From here, everything is downhill.

$$\begin{array}{c}
 (\text{CH}_3)_3\text{NH}^+ \xrightleftharpoons{K_a} (\text{CH}_3)_3\text{N} + \text{H}^+ \\
 \text{F} \quad -x \qquad \qquad x \qquad x \\
 \\
 \frac{x^2}{0.050 - x} = 1.59 \times 10^{-10} \qquad (9-12) \\
 \\
 x = 2.8 \times 10^{-6} \text{ M} \Rightarrow \text{pH} = 5.55
 \end{array}$$

TEST YOURSELF Find the pH of 0.050 M triethylammonium bromide. (*Answer:* 6.01)

9-2:Weak Acids and Bases

- For the reaction $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$, a certain fraction of the initial concentration of the weak acid (F) exists as the conjugate base A^- . This is known as the **fraction of dissociation (α)**.
- The fraction of dissociation, α , is given by:

$$\alpha = \frac{[\text{A}^-]}{[\text{A}^-] + [\text{HA}]} = \frac{x}{x + (F - x)} = \frac{x}{F}$$

- Where $x = [\text{A}^-] = [\text{H}^+]$ and $[\text{HA}] = F - x$

9-2: Weak Acids and Bases

- What is the fraction of dissociation for a 0.05 M solution of trimethyl ammonium chloride ($K_a = 1.59 \times 10^{-10}$).
- Start with the reaction and the definition:



$F - x$

x

x

From the previous example, we found that the $[\text{A}^-] = 2.8 \times 10^{-6} \text{ M}$.

$$\alpha = \frac{[\text{A}^-]}{[\text{HA}] + [\text{A}^-]} \approx \frac{x}{F} = \frac{2.8 \times 10^{-6} \text{ M}}{0.05 \text{ M}} = 5.6 \times 10^{-5}$$

Only a very small fraction of the initial weak acid exists as the conjugate base.

9-2: Weak Acids and Bases

- The amount of weak acid that exists in the conjugate base form depends on the pH of the solution.
- From the K_a expression we can derive the relationship between $[H^+]$ and the α value.
- Start with K_a and the definition of alpha:

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \text{rearranging} \quad \frac{K_a}{[H^+]} = \frac{[A^-]}{[HA]} \quad \text{or} \quad [H^+]/K_a = [HA]/[A^-]$$

$K_a = 1.59 \times 10^{-10}$

$$\alpha = \frac{[A^-]}{[HA] + [A^-]} = \frac{1}{\frac{[HA]}{[A^-]} + 1} = \frac{1}{\frac{[H^+]}{K_a} + 1}$$

$$\alpha = \frac{1}{\frac{[H^+]}{K_a} + 1} \quad \text{For } \alpha = 0.5 = \frac{1}{\frac{[H^+]}{1.59 \times 10^{-10}} + 1}$$

In order for α to be 0.5 or higher, the H^+ concentration must be no higher than

9-2:Weak Acids and Bases

- **Calculating the pH for a weak base**
- For the reaction $B + H_2O \rightleftharpoons BH^+ + OH^-$, we set up and solve the equation $K_b = x^2/(F - x)$,

$$\frac{[BH^+][OH^-]}{[B]} = \frac{x^2}{F - x} = K_b$$

where $[OH^-] = [BH^+] = x$, and $[B] = F - x$.

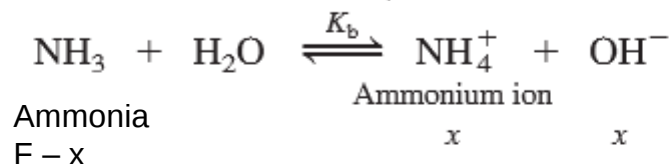
- K_b can be calculated from K_a using the relationship $K_a \times K_b = K_w$ (for a conjugate acid-base pair).

9-3: Weak-Acid Equilibria

EXAMPLE A Weak-Base Problem

Find the pH of 0.10 M ammonia.

Solution When ammonia is dissolved in water, its reaction is



In Appendix G, we find ammonium ion, NH_4^+ , listed next to ammonia. pK_a for ammonium ion is 9.245. Therefore, K_b for NH_3 is

$$K_b = \frac{K_w}{K_a} = \frac{10^{-14.00}}{10^{-9.245}} = 1.76 \times 10^{-5}$$

To find the pH of 0.10 M NH_3 , we set up and solve the equation

$$\begin{aligned} \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} &= \frac{x^2}{0.10 - x} = K_b = 1.76 \times 10^{-5} \\ x &= [\text{OH}^-] = 1.3_2 \times 10^{-3} \text{ M} \\ [\text{H}^+] &= \frac{K_w}{[\text{OH}^-]} = 7.6 \times 10^{-12} \text{ M} \Rightarrow \text{pH} = -\log[\text{H}^+] = 11.12 \end{aligned}$$

TEST YOURSELF Find the pH of 0.10 M methylamine. (*Answer:* 11.80)

9-5: Buffers

- **Buffers:** A buffer is a mixture of a **weak acid** and its **conjugate base**.
- It resists changes in pH because it reacts with added acid or base.
- For the dissociation of a weak acid $HA \rightleftharpoons H^+ + A^-$

The pH is given by the Henderson-Hasselbalch equation:

$$pH = pK_a + \text{Log} \left(\frac{[A^-]}{[HA]} \right)$$

Note: A red arrow points from the text $pK_a = -\text{Log } K_a$ to the pK_a term in the equation.

where pK_a *applies to the species in the denominator.*

- The *concentrations* of HA and A^- are essentially unchanged from those used to prepare the solution.

9-5: Buffers

EXAMPLE Using the Henderson-Hasselbalch Equation

Sodium hypochlorite (NaOCl , the active ingredient of almost all bleaches) was dissolved in a solution buffered to pH 6.20. Find the ratio $[\text{OCl}^-]/[\text{HOCl}]$ in this solution.

Solution In Appendix G, we find that $\text{p}K_a = 7.53$ for hypochlorous acid, HOCl . The pH is known, so the ratio $[\text{OCl}^-]/[\text{HOCl}]$ can be calculated from the Henderson-Hasselbalch equation.

$$\begin{aligned}\text{HOCl} &\rightleftharpoons \text{H}^+ + \text{OCl}^- \\ \text{pH} &= \text{p}K_a + \log \frac{[\text{OCl}^-]}{[\text{HOCl}]} \\ 6.20 &= 7.53 + \log \frac{[\text{OCl}^-]}{[\text{HOCl}]} \\ -1.33 &= \log \frac{[\text{OCl}^-]}{[\text{HOCl}]} \\ 10^{-1.33} &= 10^{\log([\text{OCl}^-]/[\text{HOCl}])} = \frac{[\text{OCl}^-]}{[\text{HOCl}]} \\ 0.047 &= \frac{[\text{OCl}^-]}{[\text{HOCl}]}\end{aligned}$$

The ratio $[\text{OCl}^-]/[\text{HOCl}]$ is set by pH and $\text{p}K_a$. We do not need to know how much NaOCl was added, or the volume.

TEST YOURSELF Find $[\text{OCl}^-]/[\text{HOCl}]$ if pH is raised by one unit to 7.20. (**Answer:** 0.47)

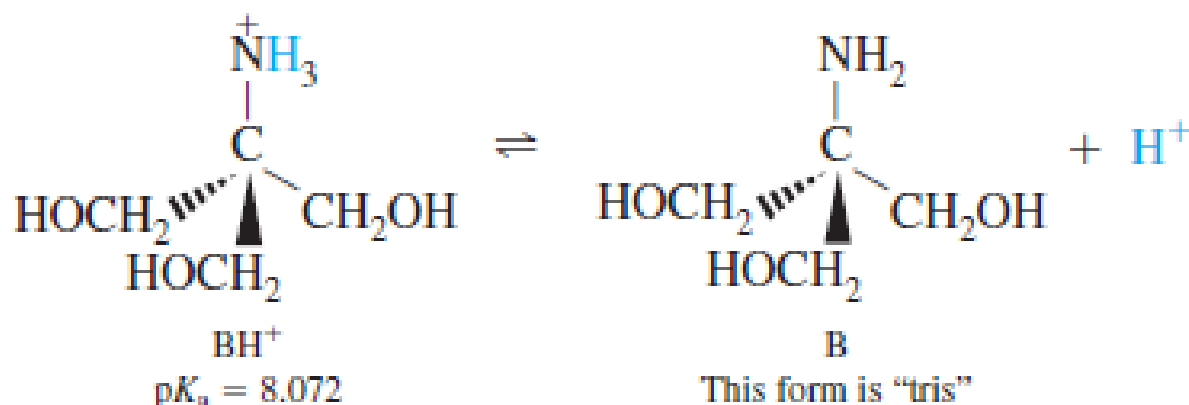
Conjugate Acids and Bases

- The conjugate base of a weak acid is a weak base. The weaker the acid, the stronger the base.
- However, if one member of a conjugate pair is weak, so is its conjugate.
- The relation between K_a for an acid and K_b for its conjugate base in aqueous solution is $K_w = K_b \times K_a$.
- When a strong acid (or base) is added to a weak base (or acid), they react nearly completely.

9-5: Buffers

A Buffer in Action

For illustration, we choose a widely used buffer called “tris,” which is short for tris(hydroxymethyl)aminomethane.



In Appendix G, we find $\text{p}K_a = 8.072$ for the conjugate acid of tris. An example of a salt containing the BH^+ cation is tris hydrochloride, which is BH^+Cl^- . When BH^+Cl^- is dissolved in water, it dissociates to BH^+ and Cl^- .



$\text{p}K_a$ of tris (BH^+) = 8.072

9.5: Buffers

EXAMPLE A Buffer Solution

Find the pH of a 1.00-L aqueous solution prepared with 12.43 g of tris (FM 121.135) plus 4.67 g of tris hydrochloride (FM 157.596). P^{ka} of tris (BH^+) = 8.072

Solution The concentrations of B and BH^+ added to the solution are

$$[B] = \frac{12.43 \text{ g/L}}{121.135 \text{ g/mol}} = 0.1026 \text{ M} \quad [BH^+] = \frac{4.67 \text{ g/L}}{157.596 \text{ g/mol}} = 0.0296 \text{ M}$$

Assuming that what we mixed stays in the same form, we plug these concentrations into the Henderson-Hasselbalch equation to find the pH:

$$pH = pK_a + \log \frac{[B]}{[BH^+]} = 8.072 + \log \frac{0.1026}{0.0296} = 8.61$$

Test Yourself Find the pH if we add another 1.00 g of tris hydrochloride. (*Answer: 8.53*)

9-5: Buffers

EXAMPLE Effect of Adding Acid to a Buffer

If we add 12.0 mL of 1.00 M HCl to the solution in the previous example, what will be the new pH? P^{ka} of tris (BH^+) = 8.072

Solution The key is to realize that, *when a strong acid is added to a weak base, they react completely to give BH^+* (Box 9-3). We are adding 12.0 mL of 1.00 M HCl, which contains $(0.012\ 0\ L)(1.00\ mol/L) = 0.012\ 0\ mol$ of H^+ . This much H^+ consumes 0.012 0 mol of B to create 0.012 0 mol of BH^+ :

	B Tris	+	H^+ From HCl	$\rightarrow BH^+$
Initial moles	0.102 6		0.012 0	0.029 6
Final moles	0.090 6		—	0.041 6
	$(0.102\ 6 - 0.012\ 0)$			$(0.029\ 6 + 0.012\ 0)$

Information in the table allows us to calculate the pH:

$$\begin{aligned} pH &= pK_a + \log \frac{\text{moles of B}}{\text{moles of } BH^+} \\ &= 8.072 + \log \frac{0.090\ 6}{0.041\ 6} = 8.41 \end{aligned}$$

The volume of the solution is irrelevant.

TEST YOURSELF Find the pH if only 6.0 instead of 12.0 mL HCl were added. (*Answer:* 8.51)

9-5: Buffers

EXAMPLE Calculating How to Prepare a Buffer Solution

How many milliliters of 0.500 M NaOH should be added to 10.0 g of tris hydrochloride to give a pH of 7.60 in a final volume of 250 mL? P^{ka} of tris (BH^+) = 8.072; FM = 157.596 g/mol

Solution The moles of tris hydrochloride are $(10.0 \text{ g})/(157.596 \text{ g/mol}) = 0.0635 \text{ mol}$. We can make a table to help solve the problem:

Reaction with OH^- : BH^+	+	OH^-	$\rightarrow$	B
Initial moles	0.0635	x		—
Final moles	$0.0635 - x$	—		x

The Henderson-Hasselbalch equation allows us to find x , because we know pH and pK_a .

$$\begin{aligned} \text{pH} &= pK_a + \log \frac{\text{mol B}}{\text{mol } BH^+} \\ 7.60 &= 8.072 + \log \frac{x}{0.0635 - x} \\ -0.472 &= \log \frac{x}{0.0635 - x} \\ 10^{-0.472} &= \frac{x}{0.0635 - x} \Rightarrow x = 0.0160 \text{ mol} \end{aligned}$$

This many moles of NaOH is contained in

$$\frac{0.0160 \text{ mol}}{0.500 \text{ mol/L}} = 0.0320 \text{ L} = 32.0 \text{ mL}$$

TEST YOURSELF How many mL of 0.500 M NaOH should be added to 10.0 g of tris hydrochloride to give a pH of 7.40 in a final volume of 500 mL? (**Answer:** 22.3 mL)

9-5: Buffers

EXAMPLE How Much Will the pH Change?

Suppose that a buffered solution contains 50 mmol of the buffer species HA and 50 mmol of the buffer species A^- . The pH will be equal to pK_a for the buffer. How much will the pH change if 20 mmol of some other acid is created by a chemical reaction?

Solution In the worst case, the acid generated by the reaction is strong enough to convert an equivalent quantity of A^- into HA. The moles of HA would then be $50 + 20 = 70$ mmol. The moles of A^- would then be $50 - 20 = 30$ mmol. The pH would be

$$pH = pK_a + \log \frac{\text{mol } A^-}{\text{mol HA}} = pK_a + \log \frac{30 \text{ mmol}}{70 \text{ mmol}} = pK_a - 0.37$$

The pH would drop by 0.37 units. If this change is acceptable, you have enough buffer.

TEST YOURSELF If, instead, 15 mmol of strong base were generated, by how much would the pH of the original buffer rise? (*Answer:* 0.27 pH units)

Mol A^- = $50 + 15 = 65$; Mol HA = $50 - 15 = 35$
Log $65/35 = 0.27$

9-5: Buffers

- The pH of a buffer is nearly independent of dilution, but **buffer capacity** increases as the concentration of buffer increases.
- Must have more moles of buffer present than there are moles of acid or base that could be introduced into the solution.
- The maximum buffer capacity for a solution is at **pH = pK_a**, *and the useful range is pH = pK_a ± 1.*

9-5: Buffers

Choosing a buffer system:

- Choose a weak acid /conjugate base system with a $pK_a \pm 1$ of desired pH.
- Look at the exponent in the K_a value (i.e., the x in the 10^{-x}). It should be close to the pH desired.
- **Example:** What weak acid would be appropriate for making a pH 10.0 buffer?
- Look at acid dissociation constants in Appendix 3. Ammonia, NH_4^+ has a K_a of 5.70×10^{-10} .

$pK_a = 9.24$. This is an appropriate buffer for a pH range of 8.24–10.24 pH units (i.e., $pK_a \pm 1$).