

G U I D E D E X P L A N A T I O N

AQA A-Level Chemistry (A2)

Acids and Bases - pH and Buffer Solutions

Specification Reference: 3.1.11.1

Learning Objectives

- 1 Define pH and calculate pH for strong acids and strong bases.
- 2 Explain the ionic product of water (K_w) and its temperature dependence.
- 3 Define weak acids and weak bases, and explain the acid dissociation constant (K_a) and base dissociation constant (K_b).
- 4 Calculate pH for weak acids and weak bases using K_a or K_b .
- 5 Describe the composition and function of buffer solutions.
- 6 Explain the mechanism of action of acidic and basic buffer solutions.
- 7 Calculate the pH of buffer solutions using the Henderson-Hasselbalch equation or ICE tables.
- 8 Explain the applications of buffer solutions in biological systems and chemical processes.

Acids and Bases - pH and Buffer Solutions

1. Introduction to pH and the Ionic Product of Water (K_w)

Acids and bases are fundamental chemical species, and their strength is often quantified using the pH scale. The pH scale provides a convenient way to express the concentration of hydrogen ions (H^+) in a solution, which dictates its acidity or alkalinity. Understanding pH is crucial for many chemical and biological processes, from maintaining physiological pH in living organisms to controlling reaction conditions in industrial chemistry. This section will introduce the concept of pH and the essential role of water's autoionization.

pH

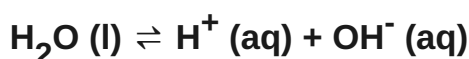
pH is a measure of the hydrogen ion concentration in an aqueous solution. It is defined as the negative base-10 logarithm of the hydrogen ion concentration, $[H^+]$, expressed in mol dm^{-3} . A lower pH indicates a higher concentration of H^+ ions and thus a more acidic solution, while a higher pH indicates a lower concentration of H^+ ions and a more alkaline solution. The pH scale typically ranges from 0 to 14 at 298 K.

$$\text{pH} = -\log_{10}[H^+]$$

Where: pH = pH value (unitless), $[H^+]$ = hydrogen ion concentration (mol dm^{-3})

The Ionic Product of Water (K_w)

Water is an amphoteric substance, meaning it can act as both an acid and a base. In pure water, a small extent of autoionization occurs, where water molecules react with each other to form hydrogen ions (H^+ , often represented as H_3O^+) and hydroxide ions (OH^-). This equilibrium is crucial for understanding the pH of neutral solutions and the relationship between $[H^+]$ and $[OH^-]$.



Where: This represents the autoionization of water.

The equilibrium constant for this reaction is called the ionic product of water, K_w . At a standard temperature of 298 K (25 °C), the value of K_w is $1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$. This value is constant for a given temperature. In pure water, $[H^+] = [OH^-]$, so at 298 K, $[H^+] = \sqrt{K_w} = \sqrt{(1.0 \times 10^{-14})} = 1.0 \times 10^{-7} \text{ mol dm}^{-3}$, which gives a pH of 7, defining neutrality.

$$K_w = [H^+][OH^-]$$

Where: K_w = ionic product of water ($\text{mol}^2 \text{ dm}^{-6}$), $[H^+]$ = hydrogen ion concentration (mol dm^{-3}), $[OH^-]$ = hydroxide ion concentration (mol dm^{-3})

Temperature Dependence of K_w

The autoionization of water is an endothermic process ($\Delta H > 0$). According to Le Chatelier's principle, increasing the temperature will shift the equilibrium position to the right, favouring the formation of more H^+ and OH^- ions. This means that K_w increases with increasing temperature. Consequently, the pH of pure water (neutrality) will decrease at higher temperatures, as $[H^+]$ increases, although the water remains neutral because $[H^+]$ still equals $[OH^-]$. For example, at 373 K (100 °C), $K_w \approx 5.5 \times 10^{-13} \text{ mol}^2 \text{ dm}^{-6}$, leading to a neutral pH of approximately 6.13.

$$pOH = -\log_{10}[OH^-]$$

Where: pOH = pOH value (unitless), $[OH^-]$ = hydroxide ion concentration (mol dm^{-3})

$$pH + pOH = pK_w$$

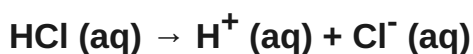
Where: $pK_w = -\log_{10}K_w$. At 298 K, $pK_w = 14$.

2. Strong Acids and Strong Bases

Strong acids and strong bases are those that dissociate completely in aqueous solution. This complete dissociation simplifies pH calculations significantly, as the concentration of H^+ or OH^- ions can be directly determined from the initial concentration of the acid or base. Understanding their behaviour is foundational before moving on to weak acids and bases.

Strong Acid

A strong acid is an acid that completely dissociates or ionises in aqueous solution to produce hydrogen ions (H^+). Examples include hydrochloric acid (HCl), nitric acid (HNO_3), and sulfuric acid (H_2SO_4). For monoprotic strong acids, the concentration of H^+ ions is equal to the initial concentration of the acid.



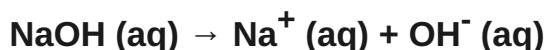
Where: This shows the complete dissociation of hydrochloric acid.

Calculating pH of Strong Acids

For a monoprotic strong acid, such as HCl, if its concentration is ' C ' mol dm^{-3} , then $[H^+] = C \text{ mol dm}^{-3}$. The pH can then be calculated directly using the pH formula. For diprotic strong acids like H_2SO_4 , it's important to consider that each molecule produces two H^+ ions, so $[H^+] = 2 \times C$, assuming complete dissociation of both protons.

Strong Base

A strong base is a base that completely dissociates in aqueous solution to produce hydroxide ions (OH^-). Examples include sodium hydroxide (NaOH), potassium hydroxide (KOH), and barium hydroxide ($\text{Ba}(\text{OH})_2$). For monobasic strong bases, the concentration of OH^- ions is equal to the initial concentration of the base.



Where: This shows the complete dissociation of sodium hydroxide.

Calculating pH of Strong Bases

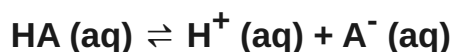
For a monobasic strong base, such as NaOH , if its concentration is ' C ' mol dm^{-3} , then $[\text{OH}^-] = C \text{ mol dm}^{-3}$. To find the pH, first calculate pOH using $\text{pOH} = -\log_{10}[\text{OH}^-]$, and then use the relationship $\text{pH} + \text{pOH} = \text{p}K_w$ (which is 14 at 298 K) to find the pH. For dibasic strong bases like $\text{Ba}(\text{OH})_2$, $[\text{OH}^-] = 2 \times C$.

3. Weak Acids and Weak Bases: K_a and K_b

Unlike strong acids and bases, weak acids and bases only partially dissociate in aqueous solution, establishing an equilibrium between the undissociated molecule and its ions. This partial dissociation means that their pH calculations are more complex and require the use of equilibrium constants, K_a for acids and K_b for bases.

Weak Acid

A weak acid is an acid that only partially dissociates or ionises in aqueous solution, establishing an equilibrium between the undissociated acid molecule and its conjugate base and hydrogen ions. Examples include ethanoic acid (CH_3COOH), carbonic acid (H_2CO_3), and hydrofluoric acid (HF). The extent of dissociation is typically very small.



Where: This represents the partial dissociation of a generic weak acid, HA.

Acid Dissociation Constant (K_a)

The acid dissociation constant, K_a , is the equilibrium constant for the dissociation of a weak acid. It quantifies the strength of a weak acid; a larger K_a value indicates a stronger weak acid (more dissociation). K_a values are typically very small, reflecting the limited dissociation of weak acids. The expression for K_a is derived from the equilibrium expression for the dissociation of a weak acid.

$$K_a = ([H^+][A^-]) / [HA]$$

Where: K_a = acid dissociation constant (mol dm^{-3}), $[H^+]$ = hydrogen ion concentration (mol dm^{-3}), $[A^-]$ = conjugate base concentration (mol dm^{-3}), $[HA]$ = undissociated acid concentration (mol dm^{-3})

$$pK_a = -\log_{10} K_a$$

Where: pK_a = pK_a value (unitless). A smaller pK_a indicates a stronger weak acid.

Weak Base

A weak base is a base that only partially dissociates or ionises in aqueous solution, establishing an equilibrium between the undissociated base molecule and its conjugate acid and hydroxide ions. Examples include ammonia (NH_3) and organic amines. The extent of dissociation is typically very small.



Where: This represents the partial dissociation of a generic weak base, B.

Base Dissociation Constant (K_b)

The base dissociation constant, K_b , is the equilibrium constant for the dissociation of a weak base. It quantifies the strength of a weak base; a larger K_b value indicates a stronger weak base (more dissociation). K_b values are typically very small. The expression for K_b is derived from the equilibrium expression for the dissociation of a weak base.

$$K_b = ([BH^+][OH^-]) / [B]$$

Where: K_b = base dissociation constant (mol dm^{-3}), $[BH^+]$ = conjugate acid concentration (mol dm^{-3}), $[OH^-]$ = hydroxide ion concentration (mol dm^{-3}), $[B]$ = undissociated base concentration (mol dm^{-3})

$$pK_b = -\log_{10} K_b$$

Where: pK_b = pK_b value (unitless). A smaller pK_b indicates a stronger weak base.

Relationship between K_a and K_b for Conjugate Acid-Base Pairs

For a conjugate acid-base pair (e.g., HA and A^- , or B and BH^+), there is a direct relationship between their K_a and K_b values. This relationship is derived from the autoionization of water and is given by $K_a \times K_b = K_w$. This means that if you know the K_a of a weak acid, you can determine the K_b of its conjugate base, and vice versa. This relationship is particularly useful when dealing with salts of weak acids or bases.

$$K_a \times K_b = K_w$$

Where: K_a = acid dissociation constant, K_b = base dissociation constant, K_w = ionic product of water

$$pK_a + pK_b = pK_w$$

Where: pK_a = pK_a value, pK_b = pK_b value, pK_w = pK_w value (14 at 298 K)

4. Calculating pH of Weak Acids and Weak Bases

Calculating the pH of weak acid and weak base solutions requires an understanding of equilibrium and often involves making simplifying assumptions. These calculations are a core skill in A-Level Chemistry and typically involve setting up an ICE (Initial, Change, Equilibrium) table or using approximations based on the small extent of dissociation.

Calculating pH of Weak Acids

For a weak acid HA, the dissociation equilibrium is $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$. We assume that the initial concentration of H^+ from water is negligible compared to that produced by the acid. At equilibrium, if 'x' mol dm^{-3} of HA dissociates, then $[H^+] = x$ and $[A^-] = x$, while $[HA] = [HA]_{initial} - x$. Since weak acids dissociate very little, we can often approximate $[HA]_{initial} - x \approx [HA]_{initial}$. This simplifies the K_a expression to $K_a \approx x^2 / [HA]_{initial}$, allowing us to calculate $x = [H^+]$ and then pH.

- **Step 1: Write the dissociation equilibrium for the weak acid.** E.g., $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$.
- **Step 2: Write the K_a expression.** $K_a = ([H^+][CH_3COO^-]) / [CH_3COOH]$.
- **Step 3: Set up an ICE table (optional but helpful).** Let $[H^+] = x$ at equilibrium. Then $[CH_3COO^-] = x$ and $[CH_3COOH] = [CH_3COOH]_{initial} - x$.
- **Step 4: Make the approximation.** For weak acids, x is usually very small compared to $[CH_3COOH]_{initial}$, so $[CH_3COOH] \approx [CH_3COOH]_{initial}$.
- **Step 5: Substitute into the K_a expression.** $K_a \approx x^2 / [CH_3COOH]_{initial}$.
- **Step 6: Solve for x.** $x = \sqrt{K_a \times [CH_3COOH]_{initial}}$. This 'x' is $[H^+]$.
- **Step 7: Calculate pH.** $pH = -\log_{10}[H^+]$.

Calculating pH of Weak Bases

For a weak base B, the dissociation equilibrium is $B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$. Similar to weak acids, we assume that the initial concentration of OH^- from water is negligible. If 'x' mol dm^{-3} of B reacts, then $[OH^-] = x$ and $[BH^+] = x$, while $[B] = [B]_{initial} - x$. We can approximate $[B]_{initial} - x \approx [B]_{initial}$. This simplifies the K_b expression to $K_b \approx x^2 / [B]_{initial}$, allowing us to calculate $x = [OH^-]$, then pOH, and finally pH.

- **Step 1: Write the dissociation equilibrium for the weak base.** E.g., $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$.
- **Step 2: Write the K_b expression.** $K_b = ([NH_4^+][OH^-]) / [NH_3]$.

- **Step 3: Set up an ICE table (optional).** Let $[\text{OH}^-] = x$ at equilibrium. Then $[\text{NH}_4^+] = x$ and $[\text{NH}_3] = [\text{NH}_3]_{\text{initial}} - x$.
- **Step 4: Make the approximation.** For weak bases, x is usually very small compared to $[\text{NH}_3]_{\text{initial}}$, so $[\text{NH}_3] \approx [\text{NH}_3]_{\text{initial}}$.
- **Step 5: Substitute into the K_b expression.** $K_b \approx x^2 / [\text{NH}_3]_{\text{initial}}$.
- **Step 6: Solve for x .** $x = \sqrt{K_b \times [\text{NH}_3]_{\text{initial}}}$. This ' x ' is $[\text{OH}^-]$.
- **Step 7: Calculate pOH.** $\text{pOH} = -\log_{10}[\text{OH}^-]$.
- **Step 8: Calculate pH.** $\text{pH} = 14 - \text{pOH}$ (at 298 K).

5. Buffer Solutions: Principles and Mechanism

Buffer solutions are critical in chemistry and biology because they resist changes in pH upon the addition of small amounts of acid or base. This ability to maintain a relatively constant pH is vital for many chemical reactions, biological processes (e.g., blood pH), and industrial applications. This section will define buffer solutions, explain their composition, and detail their mechanism of action.

Buffer Solution

A buffer solution is a solution that resists changes in pH when small amounts of acid or base are added. It typically consists of a mixture of a weak acid and its conjugate base, or a weak base and its conjugate acid. The components of the buffer system are in equilibrium, allowing them to neutralise added H^+ or OH^- ions.

Composition of Buffer Solutions

There are two main types of buffer solutions, depending on whether they are designed to operate in acidic or alkaline pH ranges:

- **Acidic Buffer:** Composed of a weak acid and a salt containing its conjugate base. For example, ethanoic acid (CH_3COOH) and sodium ethanoate (CH_3COONa). The weak acid provides HA , and the salt provides A^- (the conjugate base).
- **Alkaline Buffer:** Composed of a weak base and a salt containing its conjugate acid. For example, ammonia (NH_3) and ammonium chloride (NH_4Cl). The weak base provides B , and the salt provides BH^+ (the conjugate acid).

Mechanism of Action of an Acidic Buffer

Consider an acidic buffer made from a weak acid (HA) and its conjugate base (A^-). The equilibrium established is: $\text{HA}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{A}^-(\text{aq})$. The key to its buffering action lies in the presence of significant concentrations of both HA and A^- .

- **Addition of Acid (H^+):** If a small amount of H^+ ions is added, the equilibrium shifts to the left. The added H^+ ions react with the conjugate base (A^-) to form the weak acid (HA): $\text{H}^+(\text{aq}) + \text{A}^-(\text{aq}) \rightarrow \text{HA}(\text{aq})$. Since HA is a weak acid, it remains largely undissociated, thus removing most of the added H^+ from the solution and preventing a significant drop in pH.

- **Addition of Base (OH^-):** If a small amount of OH^- ions is added, the equilibrium shifts to the right. The added OH^- ions react with the weak acid (HA) to form water and the conjugate base (A^-): $\text{OH}^- (\text{aq}) + \text{HA} (\text{aq}) \rightarrow \text{H}_2\text{O} (\text{l}) + \text{A}^- (\text{aq})$. This removes most of the added OH^- from the solution, preventing a significant rise in pH.

Mechanism of Action of an Alkaline Buffer

Consider an alkaline buffer made from a weak base (B) and its conjugate acid (BH^+). The equilibrium established is: $\text{B} (\text{aq}) + \text{H}_2\text{O} (\text{l}) \rightleftharpoons \text{BH}^+ (\text{aq}) + \text{OH}^- (\text{aq})$. Again, significant concentrations of both B and BH^+ are present.

- **Addition of Acid (H^+):** If a small amount of H^+ ions is added, the H^+ ions react with the weak base (B) to form the conjugate acid (BH^+): $\text{H}^+ (\text{aq}) + \text{B} (\text{aq}) \rightarrow \text{BH}^+ (\text{aq})$. This removes most of the added H^+ from the solution, preventing a significant drop in pH.
- **Addition of Base (OH^-):** If a small amount of OH^- ions is added, the equilibrium shifts to the left. The added OH^- ions react with the conjugate acid (BH^+) to form the weak base (B) and water: $\text{OH}^- (\text{aq}) + \text{BH}^+ (\text{aq}) \rightarrow \text{B} (\text{aq}) + \text{H}_2\text{O} (\text{l})$. This removes most of the added OH^- from the solution, preventing a significant rise in pH.

Buffer Capacity

Buffer capacity refers to the amount of acid or base that a buffer solution can neutralise before its pH changes significantly. It depends on the concentrations of the weak acid/base and its conjugate base/acid. A higher concentration of buffer components leads to a greater buffer capacity. The buffer is most effective when the concentrations of the weak acid and its conjugate base (or weak base and its conjugate acid) are approximately equal, i.e., when $\text{pH} \approx \text{pK}_a$ (for acidic buffers) or $\text{pOH} \approx \text{pK}_b$ (for alkaline buffers).

6. Calculating pH of Buffer Solutions

Calculating the pH of buffer solutions is a common task that can be approached using the K_a expression directly or by using the Henderson-Hasselbalch equation, which is a rearranged form of the K_a expression. Both methods rely on the initial concentrations of the weak acid/base and its conjugate.

Using the K_a Expression for Acidic Buffers

For an acidic buffer (HA/A^-), the K_a expression is $K_a = ([\text{H}^+][\text{A}^-]) / [\text{HA}]$. In a buffer solution, the concentrations of HA and A^- are significant and can be considered to be their initial concentrations, as the dissociation of HA is suppressed by the common ion A^- , and the hydrolysis of A^- is suppressed by HA. Therefore, we can rearrange the K_a expression to solve for $[\text{H}^+]$: $[\text{H}^+] = K_a \times ([\text{HA}] / [\text{A}^-])$. Once $[\text{H}^+]$ is known, pH can be calculated.

- **Step 1: Write the K_a expression.** $K_a = ([\text{H}^+][\text{A}^-]) / [\text{HA}]$.
- **Step 2: Rearrange to find $[\text{H}^+]$.** $[\text{H}^+] = K_a \times ([\text{HA}] / [\text{A}^-])$.
- **Step 3: Substitute concentrations.** Use the initial concentrations of the weak acid ($[\text{HA}]$) and its conjugate base ($[\text{A}^-]$) from the salt.
- **Step 4: Calculate pH.** $\text{pH} = -\log_{10}[\text{H}^+]$.

The Henderson-Hasselbalch Equation (for Acidic Buffers)

The Henderson-Hasselbalch equation is a convenient logarithmic form of the K_a expression, specifically designed for calculating the pH of buffer solutions. It is derived by taking the negative logarithm of both sides of the rearranged K_a expression. This equation is widely used due to its simplicity.

$$\text{pH} = \text{p}K_a + \log_{10}([A^-] / [HA])$$

Where: pH = pH value (unitless), $\text{p}K_a = -\log_{10}K_a$ (unitless), $[A^-]$ = concentration of conjugate base (mol dm^{-3}), $[HA]$ = concentration of weak acid (mol dm^{-3})

- **Step 1: Determine $\text{p}K_a$.** If K_a is given, calculate $\text{p}K_a = -\log_{10}K_a$.
- **Step 2: Identify concentrations.** Determine the concentrations of the weak acid ($[HA]$) and its conjugate base ($[A^-]$). These are usually the initial concentrations.
- **Step 3: Substitute into the Henderson-Hasselbalch equation.** $\text{pH} = \text{p}K_a + \log_{10}([A^-] / [HA])$.
- **Step 4: Calculate pH.**

Calculating pH of Alkaline Buffers

For alkaline buffers (B/BH^+), we can use a similar approach but focusing on K_b and $[OH^-]$. The K_b expression is $K_b = ([BH^+][OH^-]) / [B]$. Rearranging for $[OH^-]$: $[OH^-] = K_b \times ([B] / [BH^+])$. After calculating $[OH^-]$, find pOH, and then $\text{pH} = 14 - \text{pOH}$ (at 298 K). Alternatively, a Henderson-Hasselbalch type equation can be used for pOH: $\text{pOH} = \text{p}K_b + \log_{10}([BH^+] / [B])$.

- **Step 1: Write the K_b expression.** $K_b = ([BH^+][OH^-]) / [B]$.
- **Step 2: Rearrange to find $[OH^-]$.** $[OH^-] = K_b \times ([B] / [BH^+])$.
- **Step 3: Substitute concentrations.** Use the initial concentrations of the weak base ($[B]$) and its conjugate acid ($[BH^+]$) from the salt.
- **Step 4: Calculate pOH.** $\text{pOH} = -\log_{10}[OH^-]$.
- **Step 5: Calculate pH.** $\text{pH} = 14 - \text{pOH}$ (at 298 K).

Effect of Adding Acid/Base to a Buffer

When a small amount of acid or base is added to a buffer, the concentrations of $[HA]$ and $[A^-]$ (or $[B]$ and $[BH^+]$) change slightly. These new concentrations must be used in the buffer pH calculation. For example, if H^+ is added to an acidic buffer, $[HA]$ increases and $[A^-]$ decreases by the amount of H^+ added. If OH^- is added, $[HA]$ decreases and $[A^-]$ increases. The change in moles of acid/base added must be accounted for before recalculating the new concentrations and then the new pH.

7. Applications of Buffer Solutions

Buffer solutions are indispensable in various fields, demonstrating their practical importance beyond theoretical chemistry. Their ability to maintain stable pH is critical for the proper functioning of biological systems and the efficiency of many industrial and laboratory processes. This section highlights some key applications.

Biological Systems

Living organisms are highly sensitive to pH changes, and maintaining a stable pH is crucial for enzyme activity, protein structure, and overall metabolic function. Buffers play a vital role in regulating pH in biological fluids.

- **Blood Plasma:** The pH of human blood is maintained within a very narrow range of 7.35 to 7.45. Deviations outside this range can be life-threatening. The primary buffer systems in blood are the carbonic acid-bicarbonate buffer ($\text{H}_2\text{CO}_3/\text{HCO}_3^-$), the phosphate buffer ($\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$), and plasma proteins.
- **Intracellular Fluid:** Inside cells, the phosphate buffer system is particularly important for maintaining pH.
- **Enzyme Activity:** Enzymes, which are biological catalysts, are highly sensitive to pH. Each enzyme has an optimum pH at which it exhibits maximum activity. Buffers ensure that the pH remains within this optimal range, preventing denaturation of the enzyme.

Chemical and Industrial Processes

Beyond biology, buffers are essential in numerous chemical and industrial applications where precise pH control is required.

- **Fermentation:** In processes like brewing beer or making yogurt, microorganisms produce acids. Buffers are used to maintain the pH within the optimal range for the microorganisms' activity and product formation.
- **Pharmaceuticals:** Many drug formulations require specific pH values for stability, solubility, and effective delivery. Buffer systems are incorporated into medications, especially intravenous solutions and eye drops, to match physiological pH.
- **Dyeing and Printing:** The pH of dye baths is critical for the proper uptake and fixation of dyes onto fabrics. Buffers ensure consistent colour results.
- **Analytical Chemistry:** Buffers are used in calibration of pH meters and in many analytical techniques, such as chromatography and electrophoresis, where pH stability is crucial for separation efficiency.
- **Photography:** Developing solutions in traditional photography often require precise pH control, maintained by buffers.

Choosing the Right Buffer

The choice of buffer depends on the desired pH range. A buffer is most effective when its pK_a (for acidic buffers) or pK_b (for alkaline buffers) is close to the target pH. The buffer capacity also needs to be considered, which relates to the concentrations of the weak acid/base and its conjugate. Generally, the effective buffering range is approximately $\text{pK}_a \pm 1$ pH unit.

Worked Examples

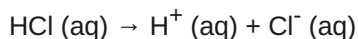
1. pH of a Strong Acid

Problem:

Calculate the pH of a $0.025 \text{ mol dm}^{-3}$ solution of hydrochloric acid (HCl) at 298 K.

Solution:

Step 1: HCl is a strong acid, so it dissociates completely.



Therefore, $[\text{H}^+] = [\text{HCl}] = 0.025 \text{ mol dm}^{-3}$.

Step 2: Use the pH formula.

$$\text{pH} = -\log_{10}[\text{H}^+]$$

Step 3: Substitute the value.

$$\text{pH} = -\log_{10}(0.025)$$

Step 4: Calculate.

$$\text{pH} = 1.60 \text{ (to 2 decimal places)}$$

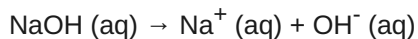
2. pH of a Strong Base

Problem:

Calculate the pH of a $0.0050 \text{ mol dm}^{-3}$ solution of sodium hydroxide (NaOH) at 298 K.

Solution:

Step 1: NaOH is a strong base, so it dissociates completely.



Therefore, $[\text{OH}^-] = [\text{NaOH}] = 0.0050 \text{ mol dm}^{-3}$.

Step 2: Calculate pOH.

$$\text{pOH} = -\log_{10}[\text{OH}^-]$$

$$\text{pOH} = -\log_{10}(0.0050) = 2.30$$

Step 3: Use the relationship $\text{pH} + \text{pOH} = 14$ (at 298 K).

$$\text{pH} = 14 - \text{pOH}$$

$$\text{pH} = 14 - 2.30$$

Step 4: Calculate.

$$\text{pH} = 11.70 \text{ (to 2 decimal places)}$$

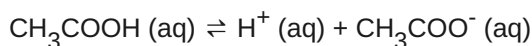
3. pH of a Weak Acid

Problem:

Calculate the pH of a 0.10 mol dm^{-3} solution of ethanoic acid (CH_3COOH) at 298 K. K_a for ethanoic acid is $1.74 \times 10^{-5} \text{ mol dm}^{-3}$.

Solution:

Step 1: Write the dissociation equilibrium and K_a expression.



$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Step 2: Let $[\text{H}^+] = x$ at equilibrium. Then $[\text{CH}_3\text{COO}^-] = x$ and $[\text{CH}_3\text{COOH}] = 0.10 - x$.

Step 3: Make the approximation: $0.10 - x \approx 0.10$ (since K_a is small).

$$\text{So, } K_a = (x \times x) / 0.10 = x^2 / 0.10$$

Step 4: Substitute K_a value and solve for x .

$$1.74 \times 10^{-5} = x^2 / 0.10$$

$$x^2 = 1.74 \times 10^{-5} \times 0.10 = 1.74 \times 10^{-6}$$

$$x = \sqrt{1.74 \times 10^{-6}} = 1.32 \times 10^{-3} \text{ mol dm}^{-3}$$

Step 5: This ' x ' is $[\text{H}^+]$. Calculate pH.

$$\text{pH} = -\log_{10}(1.32 \times 10^{-3})$$

$$\text{pH} = 2.88 \text{ (to 2 decimal places)}$$

4. pH of an Acidic Buffer Solution

Problem:

Calculate the pH of a buffer solution containing 0.20 mol dm^{-3} ethanoic acid (CH_3COOH) and 0.10 mol dm^{-3} sodium ethanoate (CH_3COONa). The K_a for ethanoic acid is $1.74 \times 10^{-5} \text{ mol dm}^{-3}$.

Solution:

Step 1: Identify the weak acid and its conjugate base concentrations.

$$[\text{CH}_3\text{COOH}] = 0.20 \text{ mol dm}^{-3}$$

$$[\text{CH}_3\text{COO}^-] = 0.10 \text{ mol dm}^{-3} \text{ (from the complete dissociation of } \text{CH}_3\text{COONa)}$$

Step 2: Calculate $\text{p}K_a$.

$$\text{p}K_a = -\log_{10}(1.74 \times 10^{-5}) = 4.76$$

Step 3: Use the Henderson-Hasselbalch equation.

$$\text{pH} = \text{p}K_a + \log_{10}([\text{A}^-] / [\text{HA}])$$

$$\text{pH} = 4.76 + \log_{10}(0.10 / 0.20)$$

$$\text{pH} = 4.76 + \log_{10}(0.50)$$

$$\text{pH} = 4.76 + (-0.30)$$

Step 4: Calculate pH.

$$\text{pH} = 4.46 \text{ (to 2 decimal places)}$$

5. pH Change in a Buffer Solution

Problem:

To the buffer solution from Worked Example 4 ($0.20 \text{ mol dm}^{-3} \text{ CH}_3\text{COOH}$ and $0.10 \text{ mol dm}^{-3} \text{ CH}_3\text{COONa}$, $K_a = 1.74 \times 10^{-5}$), 0.005 mol of HCl is added to 1.0 dm^3 of the buffer. Calculate the new pH.

Solution:

Step 1: Calculate initial moles of acid and conjugate base in 1.0 dm^3 .

Moles of $\text{CH}_3\text{COOH} = 0.20 \text{ mol}$

Moles of $\text{CH}_3\text{COO}^- = 0.10 \text{ mol}$

Step 2: HCl is a strong acid, so it adds 0.005 mol of H^+ .

H^+ reacts with the conjugate base: $\text{H}^+ + \text{CH}_3\text{COO}^- \rightarrow \text{CH}_3\text{COOH}$

Step 3: Calculate new moles after adding HCl .

New moles of $\text{CH}_3\text{COO}^- = 0.10 - 0.005 = 0.095 \text{ mol}$

New moles of $\text{CH}_3\text{COOH} = 0.20 + 0.005 = 0.205 \text{ mol}$

Step 4: Since the volume is 1.0 dm^3 , the new concentrations are:

$[\text{CH}_3\text{COO}^-] = 0.095 \text{ mol dm}^{-3}$

$[\text{CH}_3\text{COOH}] = 0.205 \text{ mol dm}^{-3}$

Step 5: Use the Henderson-Hasselbalch equation ($\text{p}K_a = 4.76$ from previous example).

$\text{pH} = \text{p}K_a + \log_{10}([\text{A}^-] / [\text{HA}])$

$\text{pH} = 4.76 + \log_{10}(0.095 / 0.205)$

$\text{pH} = 4.76 + \log_{10}(0.4634)$

$\text{pH} = 4.76 + (-0.33)$

Step 6: Calculate the new pH.

$\text{pH} = 4.43$ (to 2 decimal places)

(Note: The pH only changed from 4.46 to 4.43, demonstrating the buffering action.)

Common Mistake

Confusing strong and weak acids/bases: Treating a weak acid as fully dissociated (like a strong acid) or vice versa will lead to incorrect pH calculations. Always check if K_a/K_b is given or implied.

Common Mistake

Incorrect use of K_w : For strong bases, students sometimes try to use K_a or directly calculate pH without first finding $[\text{OH}^-]$ and then pOH. Remember $K_w = [\text{H}^+][\text{OH}^-]$ and $\text{pH} + \text{pOH} = \text{p}K_w$.

Common Mistake

Errors in buffer calculations: Forgetting to account for the change in moles of the weak acid and conjugate base when acid or base is added to a buffer. Also, incorrectly identifying which component reacts with the added acid/base.

Common Mistake

Logarithm errors: Miscalculating negative logarithms or using the wrong base for the logarithm (e.g., natural log instead of base 10).

Common Mistake

Ignoring the common ion effect: In buffer solutions, the presence of the conjugate base (from the salt) suppresses the dissociation of the weak acid, and vice versa. This is why the initial concentrations can be used in the Henderson-Hasselbalch equation.

Exam Tips

Exam Tip

Show all working: Even if you make a calculation error, marks can be awarded for correct steps and formulas. Clearly state the equation you are using.

Exam Tip

Units: Always include correct units for concentrations (mol dm^{-3}) and K_a/K_b (mol dm^{-3}). pH and $\text{p}K_a/\text{p}K_b$ are unitless.

Exam Tip

Significant figures/decimal places: Pay attention to the number of significant figures in the given data and round your final answer appropriately (usually 2 decimal places for pH).

Exam Tip

Approximations: When calculating pH of weak acids/bases, clearly state the assumption that $[\text{HA}]_{\text{initial}} - x \approx [\text{HA}]_{\text{initial}}$ or $[\text{B}]_{\text{initial}} - x \approx [\text{B}]_{\text{initial}}$. This is valid when the acid/base is very weak or its concentration is relatively high (typically if $[\text{HA}]_{\text{initial}} / K_a > 400$).

Exam Tip

Buffer calculations: Remember to use moles when adding acid or base to a buffer, then convert back to concentrations if the volume changes or if the Henderson-Hasselbalch equation is used with concentrations.

Exam Tip

K_w and temperature: Be aware that K_w (and thus $\text{p}K_w$ and the neutral pH) changes with temperature. Unless specified, assume 298 K (25 °C) where $K_w = 1.0 \times 10^{-14}$ and neutral pH = 7.

Comparison of Strong and Weak Acids/Bases

Feature	Strong Acid/Base	Weak Acid/Base
Dissociation in Water	Complete (100%)	Partial (equilibrium established)
Equilibrium Constant	Not applicable (reaction goes to completion)	K_a (for acids) or K_b (for bases)
$[H^+]$ or $[OH^-]$ relative to initial concentration	Equals initial concentration (for monoprotic/monobasic)	Much less than initial concentration
pH Calculation	Directly from initial concentration	Requires K_a/K_b and equilibrium calculations (e.g., ICE table or approximation)
Conductivity	High (many ions)	Low (few ions)
Reaction with Metals/Carbonates	Vigorous	Slow/moderate

Summary

The pH scale quantifies the acidity or alkalinity of a solution, defined as $pH = -\log_{10}[H^+]$. Water undergoes autoionization, described by the ionic product $K_w = [H^+][OH^-]$, which is $1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ at 298 K. K_w is temperature-dependent, increasing with temperature. Strong acids and bases dissociate completely, allowing direct calculation of $[H^+]$ or $[OH^-]$ from their initial concentrations. Weak acids and bases, however, only partially dissociate, establishing an equilibrium. Their strengths are quantified by the acid dissociation constant (K_a) and base dissociation constant (K_b), respectively. pH calculations for weak acids and bases involve using K_a or K_b in equilibrium expressions, often with simplifying approximations. Buffer solutions resist pH changes upon addition of small amounts of acid or base. They consist of a weak acid and its conjugate base (acidic buffer) or a weak base and its conjugate acid (alkaline buffer). Their buffering action relies on the equilibrium between these components to neutralise added H^+ or OH^- ions. The pH of a buffer can be calculated using the K_a expression or the Henderson-Hasselbalch equation: $pH = pK_a + \log_{10}([A^-]/[HA])$. Buffers are crucial in biological systems (e.g., blood pH regulation) and various industrial and laboratory processes where precise pH control is essential.