Reactivity 3.1 HL

IB CHEMISTRY HL

25	16		6	2	25
Mn	**S**	**J**	**C**	**He**	**Mn**
Manganese	Sulfur		Carbon	Helium	Manganese
54.938045	32.065		12.0107	4.002602	54.938045

Reactivity 3.1.9

Understandings:

- The pOH scale describes the $[OH^-]$ of a solution.
  $pOH = -\log_{10}[OH^-]$; $[OH^-] = 10^{-pOH}$

Learning outcomes:

- Interconvert $[H^+]$, $[OH^-]$, pH and pOH values.

Additional notes:

- The equations for pOH are given in the data booklet.

pOH scale

- The pOH scale gives a measure of the $[OH^-]$ ions in solution.

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

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

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

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

- The pOH scale in inverse, which means the higher the $[OH^-]$, lower the pOH value.
- The relationship between pH and pOH is:

$$pH + pOH = 14.00 \text{ at } 298 \text{ K}$$

Exercises:

1) A solution has a pH of 2.90 at 298 K. Calculate the $[H^+]$, $[OH^-]$ and pOH.

2) A solution at 298 K has a $[H^+]$ of 4.60×10^{-8} mol dm^{-3}. Calculate the $[OH^-]$ and pOH of the solution.

Reactivity 3.1.10

Understandings:

- The strengths of weak acids and bases are described by their K_a, K_b, pK_a or pK_b values.

Learning outcomes:

- Interpret the relative strengths of acids and bases from these data.

Acid dissociation constant, K_a

- K_a is an equilibrium constant that refers to the dissociation or ionisation of an acid.
- H_2O is not included in the K_a expression as it is a constant.

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- The magnitude of the K_a tells us the extent of dissociation and the strength of the acid.
- The larger the value of the K_a, the further the equilibrium position lies to the right and the stronger the acid.

Base dissociation constant, K_b

- K_b is an equilibrium constant that refers to the dissociation or ionisation of a base.

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

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

- The magnitude of the K_b tells us the extent of dissociation and the strength of the base.
- The larger the value of the K_b, the further the equilibrium position lies to the right, and the stronger the base.

Exercise: Write expressions for the K_a or K_b for the following reactions.

1) $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$

2) $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

pK_a and pK_b

$$pK_a = -\log_{10}K_a \qquad pK_b = -\log_{10}K_b$$

$$K_a = 10^{-pK_a} \qquad K_b = 10^{-pK_b}$$

- pK_a and pK_b values are usually positive and have no units.
- A change in one unit of pK_a or pK_b represents a ten-fold change in the value K_a or K_b.

K_a and pK_a

- K_a and pK_a have an inverse relationship; the stronger the acid, the higher the value of K_a and the lower the value of the pK_a.

K_b and pK_b

- K_b and pK_b have an inverse relationship; the stronger the base, the higher the value of K_b and the lower the value of the pK_b.

Exercise: The following table shows pK_a and pK_b values for acids and bases. Identify the strongest acid and the strongest base from the table.

Acid	**pK_a**	**Base**	**pK_b**
Methanoic acid	3.75	Ammonia	4.75
Ethanoic acid	4.76	Methylamine	3.34

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Understandings:

- For a conjugate acid–base pair, the relationship $K_a \times K_b = K_w$ can be derived from the expressions for K_a and K_b.

Learning outcomes:

- Solve problems involving these values.

Additional notes:

- The use of quadratic equations is not expected in calculations.

Linking questions:

- Reactivity 2.3 How can we simplify calculations when equilibrium constants K_a and K_b are very small?

Relationship between K_a, K_b and K_w

$$K_a \times K_b = \frac{[H_3O^+][A^-]}{[HA]} \times \frac{[BH^+][OH^-]}{[B]} = [H^+][OH^-]$$

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

$K_w = K_a \times K_b$

- For a conjugate acid-base pair, $K_a \times K_b = 1.00 \times 10^{-14}$ at 298 K

Exercises:

1) The K_a of CH_3COOH is 1.74×10^{-5}. Determine the K_b for its conjugate base CH_3COO^- at 298 K.

2) The K_b of $C_6H_5NH_2$ is 7.41×10^{-10}. Determine the K_a for its conjugate acid $C_6H_5NH_3^+$ at 298 K.

3) The pK_b of CH_3NH_2 is 3.34. Determine the K_a for its conjugate acid $CH_3NH_3^+$ at 298 K.

Calculating K_a or K_b of a weak acid or weak base

Example 1: A 0.100 mol dm^{-3} solution of HClO has a pH of 4.23. Calculate the K_a of HClO.

$$HClO(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$$

Example 2: A 0.100 mol dm^{-3} solution of $C_6H_5NH_2$ has a pH of 8.79. Calculate the K_b of $C_6H_5NH_2$.

$$C_6H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_3^+(aq) + OH^-(aq)$$

Calculating the pH of a weak acid or weak base

Example 1: Propanoic acid, CH_3CH_2COOH, is a weak acid. Calculate the pH of a 0.0500 mol dm^{-3} solution of propanoic acid at 298 K. The pK_a of propanoic acid is 4.87.

Example 2: Ammonia, NH_3, is a weak base. Calculate the pH of a 0.0250 mol dm^{-3} solution of ammonia at 298 K. The pK_b of ammonia is 4.75.

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Understandings:

- The pH of a salt solution depends on the relative strengths of the parent acid and base.

Learning outcomes:

- Construct equations for the hydrolysis of ions in a salt and predict the effect of each ion on the pH of the salt solution.

Additional notes:

- Examples should include the ammonium ion, the carboxylate ion, the carbonate ion and the hydrogen carbonate ion.
- The acidity of hydrated transition element ions and $Al^{3+}(aq)$ is not required.

Salt hydrolysis

- Salt hydrolysis is the reaction of a cation or an anion with water which ionises the water molecule into H^+ and OH^-.
- This results in the formation of either an acidic solution or a basic solution.
- Anion hydrolysis results in a solution with pH > 7 due to the production of OH^- ions.

$$A^-(aq) + H_2O(l) \rightarrow HA(aq) + OH^-(aq)$$

- Cation hydrolysis results in a solution with pH < 7 due to the production of H^+ ions.

$$M^+(aq) + H_2O(l) \rightarrow MOH(aq) + H^+(aq)$$

Salt of a strong acid and strong base

- The salt formed from a strong acid and a strong base has a pH of 7 at 298 K.
- Example – the reaction between HCl and NaOH produces NaCl which is a neutral salt.
- Neither ion (Na+ or Cl^-) is able to hydrolyse water.

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

Salt of a weak acid and strong base

- The salt formed from a weak acid and a strong base has a pH of > 7 at 298 K.
- Example – the reaction between CH_3COOH and NaOH produces CH_3COONa which is a basic salt.
- The CH_3COO^- ion is able to hydrolyse water resulting in the formation of OH^- ions.

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

- The carbonate ion and hydrogen carbonate ion can also hydrolyse water to produce OH^- ions.

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3^{2-}(aq) + OH^-(aq)$$

Salt of a strong acid and weak base

- The salt formed from a strong acid and a weak base has a pH of < 7 at 298 K.
- Example – the reaction between HCl and NH_3 produces NH_4Cl which is an acidic salt.
- The NH_4^+ ion is able to hydrolyse water resulting in the formation of H^+ ions.

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_4OH(aq) + H^+(aq)$$

Exercise: Classify each of the following salts as acidic, basic or neutral, giving a reason for your choice. For each acidic or basic salt, write the equation for the hydrolysis reaction with water.

1) KBr

2) CH_3COONa

3) NH_4Cl

4) Na_2CO_3

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Understandings:

- pH curves of different combinations of strong and weak monoprotic acids and bases have characteristic shapes and features.

Learning outcomes:

- Interpret the general shapes of pH curves for all four combinations of strong and weak acids and bases.

Additional notes:

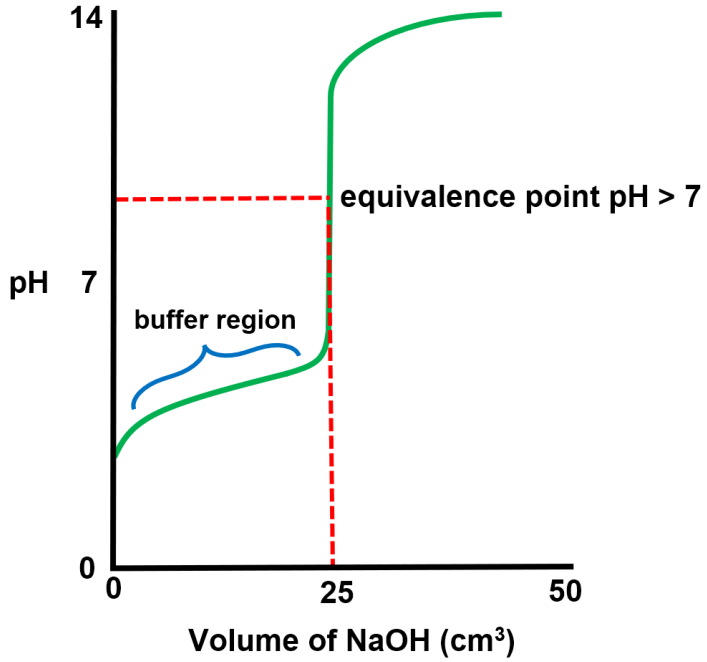
- Interpretation should include: intercept with the pH axis, equivalence point, buffer region, points where pH = pK_a or pOH = pK_b.

pH curves

- The equivalence point occurs when stoichiometrically equivalent amounts of acid and base have reacted (the solution contains only salt and water).
- The pH of the equivalence point depends on whether the salt produced is acidic or basic (salt hydrolysis).
- The end-point is the pH at which an indicators changes colour.

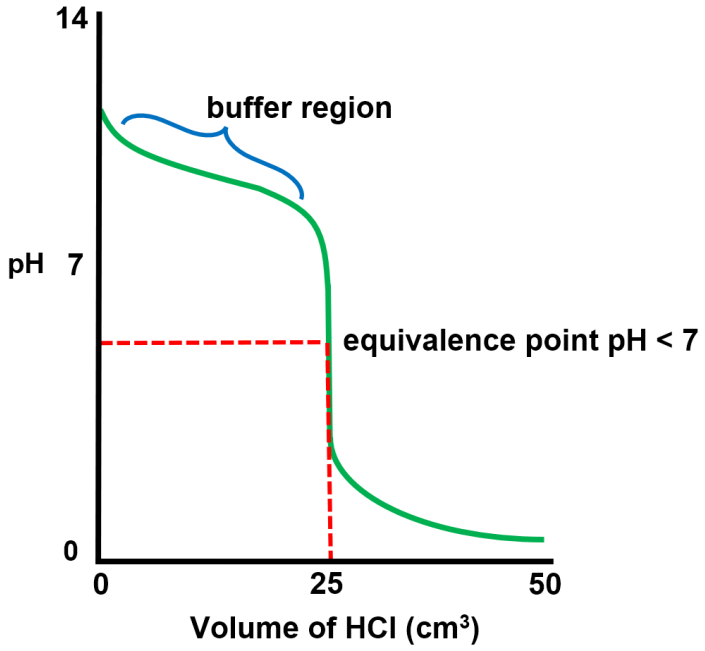
- The buffer region on a pH curve represents the region where small additions of acid or base result in little or no change in pH.

Addition of a strong base to a weak acid



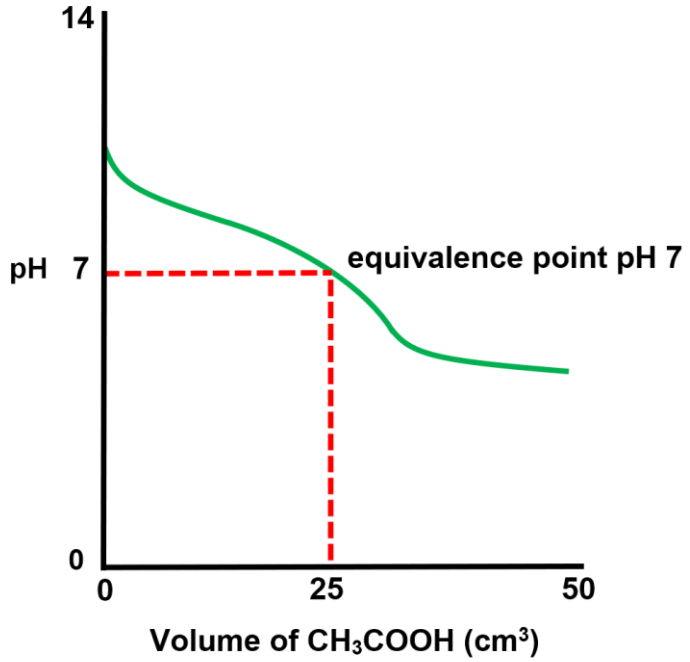
For a weak acid and strong base pH curve, there is a buffer region where the solution is resisting a change in pH.
The equivalence point is at pH > 7.

Addition of a strong acid to a weak base

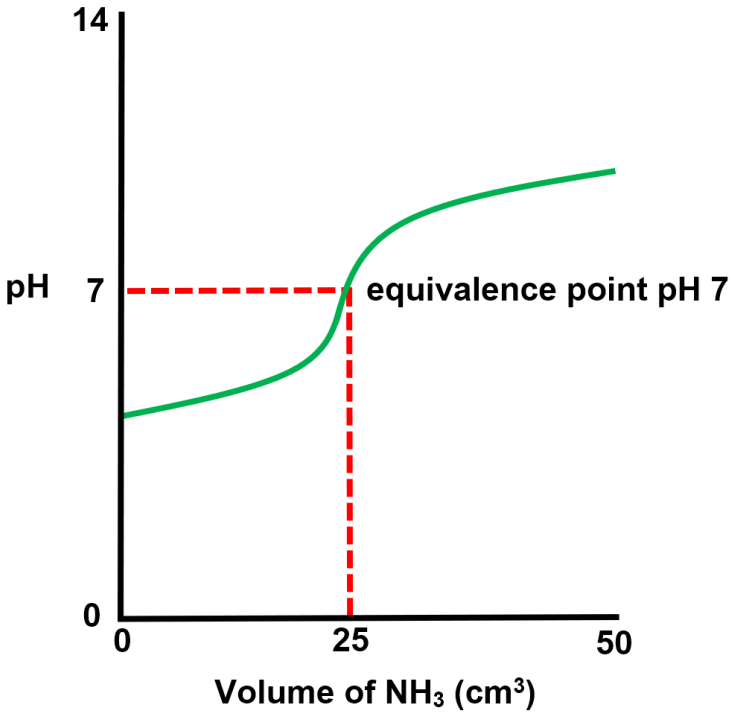


For a weak base and strong acid pH curve, there is a buffer region where the solution is resisting a change in pH.
The equivalence point is at pH < 7.

Addition of a weak acid to a weak base



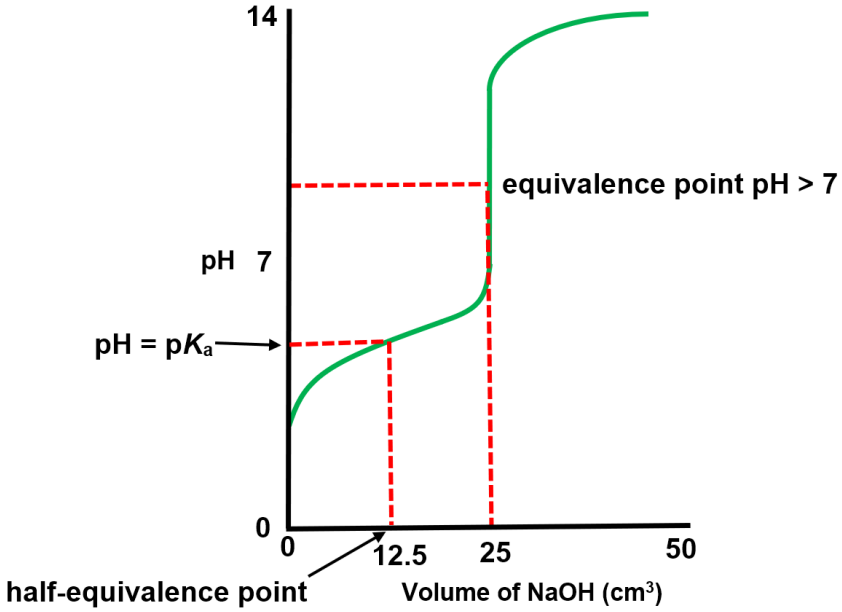
Addition of a weak base to a weak acid



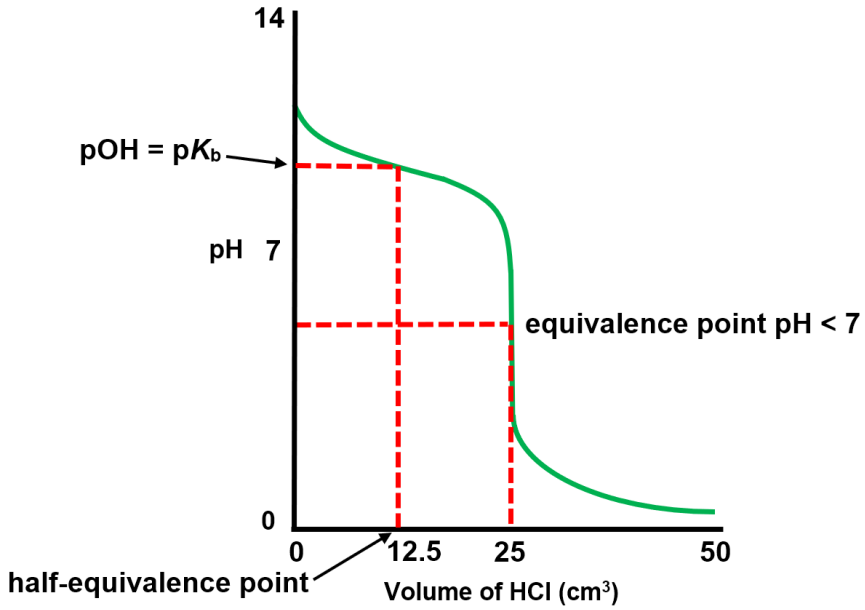
Half-equivalence point

- The half-equivalence point is the point where half the acid (or base) has been neutralised by base (or acid) and converted into salt.
- At the half-equivalence point, the pH is equal to the pK_a and the pOH is equal to the pK_b.

Addition of strong base to weak acid



Addition of strong acid to weak base



Reactivity 3.1.14 and 3.1.15

Understandings:

- Acid–base indicators are weak acids, where the components of the conjugate acid–base pair have different colours (3.1.14).
- The pH of the end point of an indicator, where it changes colour, approximately corresponds to its pK_a value (3.1.14).
- An appropriate indicator for a titration has an end point range that coincides with the pH at the equivalence point (3.1.15).

Learning outcomes:

- Construct equilibria expressions to show why the colour of an indicator changes with pH (3.1.14).
- Identify an appropriate indicator for a titration from the identity of the salt and the pH range of the indicator (3.1.15).

Additional notes:

- The generalised formula HInd(aq) can be used to represent the undissociated form of an indicator.
- Examples of indicators with their pH range are given in the data booklet.
- Include universal indicator as a mixture of many indicators with a wide pH range of colour change.
- Distinguish between the terms “end point” and “equivalence point”.

Acid-base indicators

- Acid-base indicators are weak acids or bases in which the undissociated form (HInd) and the dissociated form (In^-) have different colours.
- Example - litmus appears red in an acidic solution and blue in an alkaline solution.

$$\underset{\text{red}}{HInd}(aq) \rightleftharpoons H^+(aq) + \underset{\text{blue}}{In^-}(aq)$$

- In acidic solutions (high $[H^+]$), the equilibrium position shifts to the left and the red colour is seen.
- In alkaline solutions (high $[OH^-]$), the equilibrium position shifts to the right and the blue colour is seen.

End point

- The end point of an indicator is the pH at which it changes colour.
- An indicator changes colour when the pH is equal to its pK_a.
- The colour change can be considered to take place over a range of p$K_a \pm 1$.
- A list of acid base indicators can be found in section 18 of the data booklet.

Exercises:

1) The indicator bromophenol blue, HInd(aq), has a form that is yellow and the $In^-(aq)$ form that is blue.

(a) Write an equation to show how bromophenol blue acts as an indicator.

(b) State and explain the colour of bromophenol blue:

(i) on the addition of a strong acid.

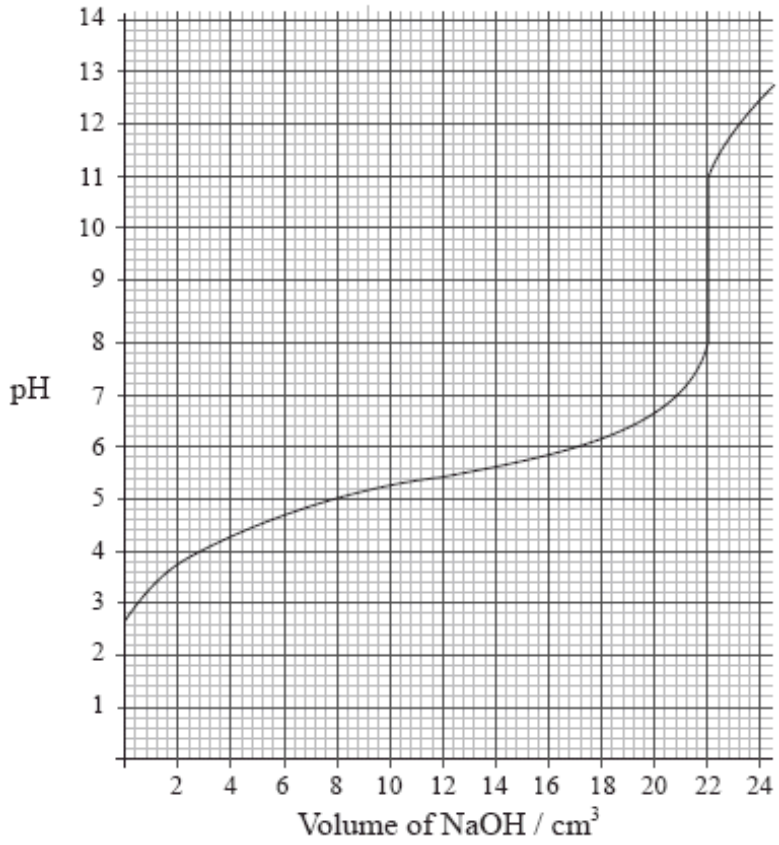
(ii) on the addition of a strong base.

2) Use the pH curve to determine the following.

(a) the pH at the equivalence point

(b) the pK_a of the weak acid

(c) a suitable indicator for the titration.



Reactivity 3.1.16

Understandings:

- A buffer solution is one that resists change in pH on the addition of small amounts of acid or alkali.

Learning outcomes:

- Describe the composition of acidic and basic buffers and explain their actions.

Linking question(s):

- Reactivity 2.3 Why must buffer solutions be composed of weak acid or base conjugate systems, not of strong acids or bases?

Buffer solutions

- Buffer solutions resist a change in pH when small amounts of acid or base are added.
- A buffer solution contains equal amounts of weak acid and conjugate base or weak base and conjugate acid.

Acidic buffers

- An acidic buffer solution can be prepared by reacting a weak acid with a strong base, ensuring that the resulting solution has equal amounts of weak acid and the salt of the weak acid and strong base.

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

1.0 mol	0.50 mol	0 mol	0 mol
0.50 mol	0 mol	0.50 mol	0.50 mol

- An acidic buffer can also be made by mixing a weak acid and the salt of the weak acid and a strong base.

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$
$$CH_3COONa(aq) \rightarrow Na^+(aq) + CH_3COO^-(aq)$$

- The resulting solution has equal amounts of weak acid, CH_3COOH, and its conjugate base CH_3COO^-.

Response to added acid

- The H^+ ions react with CH_3COO^- ions to form CH_3COOH.

$$CH_3COO^-(aq) + H^+(aq) \rightleftharpoons CH_3COOH(aq)$$

Response to added base

- The OH^- ions react with CH_3COOH to form CH_3COO^- and H_2O.

$$CH_3COOH(aq) + OH^-(aq) \rightleftharpoons CH_3COO^-(aq) + H_2O(l)$$

Basic buffers

- A basic buffer solution can be prepared by reacting a weak base with a strong acid, ensuring that the resulting solution has equal amounts of weak base and the salt of the weak base and strong acid.

$$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$$

1.0 mol	0.50 mol	0 mol
0.50 mol	0 mol	0.50 mol

- A basic buffer can also be made by mixing a weak base and the salt of the weak base and a strong acid.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
$$NH_4Cl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

- The resulting solution has equal amounts of weak base, NH_3, and its conjugate acid NH_4^+.

Response to added acid

- The H^+ ions react with NH_3 to form NH_4^+.

$$NH_3(aq) + H^+(aq) \rightleftharpoons NH_4^+(aq)$$

Response to added base

- The OH^- ions react with NH_4^+ to form NH_3 and H_2O.

$$NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O(l)$$

Reactivity 3.1.17

Understandings:

- The pH of a buffer solution depends on both:
  the pK_a or pK_b of its acid or base
  the ratio of the concentration of acid or base to the concentration of the conjugate base or acid.

Learning outcomes:

- Solve problems involving the composition and pH of a buffer solution, using the equilibrium constant.

Additional information:

- Include explanation of the effect of dilution of a buffer.

Linking question(s):

- Reactivity 2.3 How does Le Châtelier's principle enable us to interpret the behaviour of indicators and buffer solutions?