FACTFILE:
GCE CHEMISTRY

4.5 ACID-BASE EQUILIBRIA

Learning Outcomes

Students should be able to:

4.5.1 use the Brønsted-Lowry theory of acids and bases to describe proton transfer in acid-based equilibria including the idea of conjugate acid-base pairs;

4.5.2 define and understand the terms K_w, K_a, pH, pK_w and pK_a, and recall the associated units where appropriate;

4.5.3 carry out calculations involving pH for strong acids, strong bases and weak acids;

4.5.4 define and understand the term buffer solution and give a qualitative explanation of how buffer solutions work;

4.5.5 calculate the pH of a buffer solution made from a weak monobasic acid and sodium hydroxide; and

4.5.6 recall how titration curves are determined by experiment.

4.5.7 use titration curves to explain the choice of indicator; predict whether a salt solution would be acidic, alkaline or neutral based on relative strengths of the parent acid and base;

4.5.8 predict whether a salt solution would be acidic, alkaline or neutral based on relative strengths of the parent acid and base;

Brønsted-Lowry theory of acids and bases

According to the acid-base theory proposed by the British chemist Lowry and the Swedish chemist Brønsted

> **A Brønsted acid is a proton donor**
>
> **A Brønsted base is a proton acceptor**

A proton is a hydrogen ion (H^+)

An acid-base equilibria involves the transfer of protons. In such equilibria the acid donates a proton to the base. Since these reactions are reversible there is an acid and base on both sides of the equation, they are called conjugate acid-base pairs.

Example 1: an acid with water

In the forward reaction HA donates a proton to the water molecule, acting as an acid and forming A^-. In the reverse reaction A^- accepts a proton from H_3O^+ and acts as a base. A^- is the conjugate base of the acid HA. The water accepts a proton and acts as a base.

Conjugate acid-base pair

$$HA \;+\; H_2O \;\rightleftharpoons\; H_3O^+ \;+\; A^-$$

acid   base   acid   base

Conjugate acid-base pair
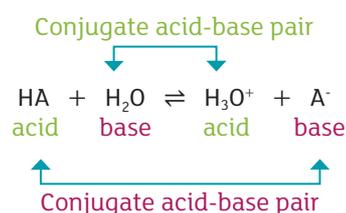
Example 2: a base with water

In solution bases accept protons from water molecules, which can then donate a proton in the reverse reaction. The water donates a proton and acts as an acid.

For example:

Conjugate acid-base pair

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
base   acid   acid   base

Conjugate acid-base pair
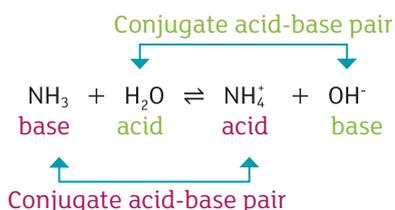
A strong acid is one which fully dissociates into ions in solution.

eg. $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$

A full arrow shows that the dissociation is complete. Hydrochloric acid is described as a strong <u>monobasic acid</u> as one mole of HCl produces one mole of $H^+(aq)$.

A monobasic acid donates one proton per molecule

A weak acid is one which partially dissociates into ions in solution.

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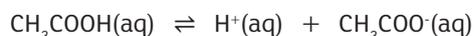
pH

The pH of a solution is the negative logarithm to base 10 of the molar hydrogen ion concentration.

$$\textbf{pH = -log}_{\textbf{10}}\textbf{[H}^+\textbf{]} \quad \text{no units}$$

To calculate the hydrogen ion concentration from the pH use

$$\textbf{[H}^+\textbf{] = 10}^{\textbf{(-pH)}}$$

Calculation of pH for strong acids

<u>Example 1</u>: What is the pH of 0.02 mol dm⁻³ H_2SO_4?

First write the equation for the dissociation of the acid, to determine the number of moles of hydrogen ions formed.

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$$
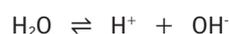
Ratio 1 H_2SO_4: $2H^+$
         0.02:   0.04

$$pH = -\log_{10}[H^+] = -\log_{10}(0.04) = 1.4$$

<u>Example 2</u>. What is the concentration of a solution of sulfuric acid which has a pH of 1.0?

$[H^+] = 10^{(-pH)}$
$[H^+] = 10^{(-1.0)} = 0.1$ mol dm⁻³
$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$
1 mol: 2 mol H^+
$[H_2SO_4] = {}^{0.1}/_2 = 0.05$ mol dm⁻³

The ionic product of water K_w

Water partially dissociates into hydrogen ions and hydroxide ions

$$H_2O \rightleftharpoons H^+ + OH^-$$

K_w is the ionic product of water

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

At 25°C, $K_w = 1.00 \times 10^{-14}$ mol² dm⁻⁶
The units of K_w are always mol² dm⁻⁶

This expression holds for all solutions at room temperature if water is present.

Also

$$pK_w = -\log_{10}K_w = 14 \text{ at } 25°C$$

Calculating pH of pure water

K_w is an equilibrium constant and varies with temperature hence the pH of pure water varies with temperature.

For pure water $[H^+] = [OH^-]$ because
$H_2O \rightleftharpoons H^+ + OH^-$

Calculate the pH of pure water at
12°C (K_w at 12 °C = 4.52×10^{-15} mol² dm⁻⁶).
$K_w = [H^+][OH^-]$ but for pure water $[H^+] = [OH^-]$ so $K_w = [H^+]^2$
$4.52 \times 10^{-15} = [H^+]^2$
$[H^+] = 6.72 \times 10^{-8}$ mol dm⁻³
$pH = -\log_{10}[H^+] = -\log_{10}(6.72 \times 10^{-8}) = 7.17$

Calculating the pH of a strong base

To calculate the pH of a strong base, use the K_w expression to find the $[H^+]$ concentration and then find the pH.

Example. Calculate the pH of a 0.1 mol dm^{-3} solution of potassium hydroxide at 298 K.
$K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6} at 298 K

$K_w = [H^+][OH^-]$
$1.00 \times 10^{-14} = [H^+] \times 0.1$

$[H^+] = 1 \times 10^{-13}$ mol dm^{-3}
pH $= -\log_{10}[H^+] = -\log_{10}(1 \times 10^{-13}) = 13$

Calculating the pH of weak acids

Weak acids dissociate partially in solution and so the hydrogen ion concentration is not the same as the concentration of the acid. To calculate the pH of a weak acid, use the acid dissociation constant K_a.

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

For a weak acid dissociation HA $\rightleftharpoons$ H$^+$ + A$^-$
K_a always has units of mol dm^{-3}.

For the weak acid $[H^+] = [A^-]$

hence
$$K_a = \frac{[H^+]^2}{[HA]}$$

and if K_a and the concentration of the acid are known, the $[H^+]$ and pH can be calculated. We assume at equilibrium that the $[HA]$ has not changed as $[H^+]$ is very small in a weak acid.

The value of K_a gives a measure of the strength of the acid. The higher the K_a, the stronger the acid Sometimes K_a values are very small and it is more convenient to record the strength of acids as pK_a values. If K_a is large then pK_a is small and the acid is strong.

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

Example

Ethanoic acid has a K_a value of 1.8×10^{-5} mol dm^{-3} at 300 K. What is the pH of a 0.10 mol dm^{-3} solution of

$$K_a = \frac{[H^+]^2}{[HA]} \qquad [HA] = 0.10 \text{ mol dm}^{-3}$$

$$1.8 \times 10^{-5} = \frac{[H^+]^2}{0.10}$$

ethanoic acid at this temperature?
$1.8 \times 10^{-5} \times 0.10 = [H^+]^2$

$[H^+] = 1.34 \times 10^{-3}$ mol dm^{-3}
pH $= -\log_{10}(1.34 \times 10^{-3}) = 2.87$

Calculating pH after neutralisation

<u>**Example**</u>: Calculate the pH of a solution resulting from mixing 25 cm^3 of 0.1 mol dm^{-3} sulfuric acid and 25 cm^3 of 0.1 mol dm^{-3} sodium hydroxide.

It is first necessary to work out the number of moles of each solution, and determine which is present in excess, and use this to find the pH.

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$
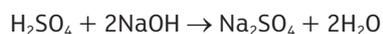
Moles of NaOH = $\dfrac{v \times c}{1000}$ = $\dfrac{25 \times 0.1}{1000}$ = 0.0025

Moles of H$_2$SO$_4$ = $\dfrac{v \times c}{1000}$ = $\dfrac{25 \times 0.1}{1000}$ = 0.0025

Ratio is 2NaOH : 1H$_2$SO$_4$
So 0.0025 mol of NaOH reacts with 0.00125 mol of H$_2$SO$_4$

The sulfuric acid is in excess by 0.0025-0.00125 = 0.00125 moles
The 0.00125 moles is dissolved in 50 cm^3 (25+25) of solution.
This is a concentration of 0.025 mol dm^{-3}

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$$

Ratio 1 H$_2$SO$_4$: 2 H$^+$
　　　 0.025 : 0.050

pH = - log$_{10}$[H$^+$] = - log$_{10}$(0.050) = 1.3

Determination of titration curves by experiment

- Place acid/base solution of known volume and concentration in a conical flask. Add 3 drops of indicator.
- Fill a burette with acid/base of known concentration.
- Add the acid/base in 5 cm^3 portions from a burette, mixing using a magnetic stirrer.
- Record the pH of the solution after each addition. (use a pH meter or narrow range pH paper)
- Add the acid/base in 1 cm^3 portions as the end point approaches
- Plot a graph of pH against volume of acid/base added. This is a titration curve.

Titration curves

The vertical region in a titration curve occurs when the correct volume of acid/alkali has been added for neutralisation. An indicator is suitable for the titration if the **rapid change in pH** at the vertical portion on the curve **overlaps with the pH range of the indicator**. There are 4 different types of titration curve. Methyl orange changes colour between pH values of 3-5 and phenolphthalein changes colour between pH values of 8-10.

1. strong acid/ strong base titration eg HCl/NaOH

   If the base is added to the acid in the conical the curve starts at pH 0-2 (strong acid) and there is a very gradual increase, until at the endpoint the pH changes rapidly from 3 and 10 and there is a vertical part on the curve. The curve ends at pH 12-14 (strong alkali).

   Any indicator which changes colour in the pH range corresponding to the vertical portion of the titration curve eg methyl orange, phenolphthalein

2. strong acid/ weak base titration eg HCl/ammonia

   If the <u>base is added to the acid</u> in the conical the curve starts at pH 0-2 (strong acid) and there is a very gradual increase, until at the endpoint the pH changes rapidly from 3 to 8 and there is a vertical part on the curve. The curve ends at pH 10 approx (weak alkali).

   Any indicator which changes colour in the pH range corresponding to the vertical portion of the titration curve is suitable eg. methyl orange is suitable but phenolphthalein is not

3. weak acid/ strong base titration eg ethanoic acid NaOH

   If the <u>base is added to the acid</u> in the conical, the curve starts at pH 3 (weak acid) and there is a very gradual increase, until at the endpoint the pH changes rapidly from 6 to 10 and there is a vertical part on the curve. The curve ends at pH 13 approx (strong alkali). Any indicator which changes colour in the pH range corresponding to the vertical portion of the titration curve eg. phenophthalein but not methyl orange.

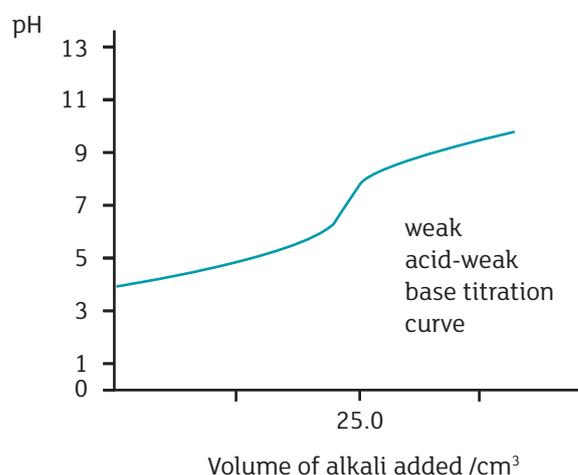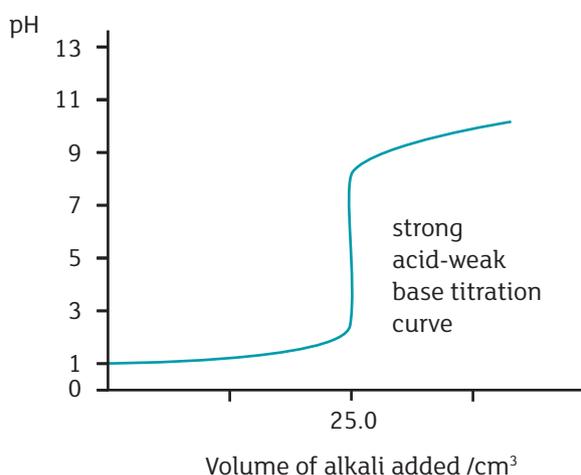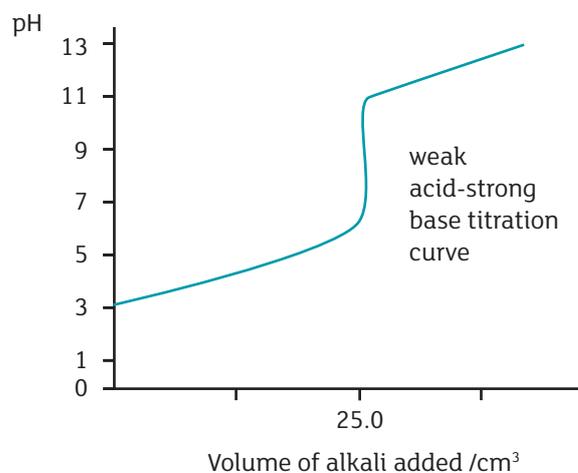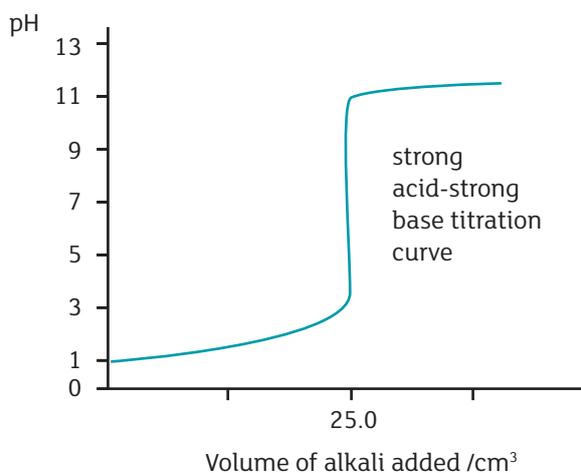4. weak acid/ weak base titration eg. ethanoic acid/ ammonia

   If the <u>base is added to the acid</u> in the conical, the curve starts at pH 3 (weak acid). There is no sharp increase in pH and no vertical part on the curve. The pH changes gradually rather than suddenly and so there is no clear end point. The curve ends at pH 11 approx (weak alkali). Weak acids and weak bases are not titrated using indicator, often a pH meter is used.

Note that if the alkali is added to the acid, then the curve is inverted. If sketching titration curves, you should always work out the volume of solution needed at the endpoint.

Phenolphthalein is colourless in acid and pink in alkali.
Methyl orange is red in acid and yellow in alkali

strong
acid-strong
base titration
curve

Volume of alkali added /cm^3

weak
acid-strong
base titration
curve

Volume of alkali added /cm^3

strong
acid-weak
base titration
curve

Volume of alkali added /cm^3

weak
acid-weak
base titration
curve

Volume of alkali added /cm^3

Buffer Solutions

A buffer solution is a solution which resists changes in pH if small amounts of acid or alkali are added to it.

An acidic buffer contains a weak acid and the salt of a weak acid, for example a solution of ethanoic acid and sodium ethanonate is a buffer.

How a buffer solution works.

In an acidic buffer containing ethanoic acid and sodium ethanoate in solution, there is

- a large amount of undissociated ethanoic acid, because it is a weak acid
- a large amount of ethanoate ions, due to the complete dissociation of the sodium ethanoate in solution.

Hence a buffer has a reservoir of ethanoic acid and ethanoate ions.

Adding acid (H$^+$) to a buffer

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$
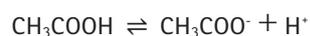
- The position of equilibrium moves to the left to remove the added H$^+$ ions
- This keeps the pH almost constant

In the buffer there is a reservoir of the ethanoate ions.

Adding alkali (OH$^-$) to a buffer

$$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$$
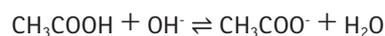
- The undissociated ethanoic acid can remove the hydroxide ions and maintain the pH.
- Or the hydroxide ions can combine with H$^+$ and form water, driving the equilibrium $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ to the right hand side to replace the H$^+$ ions and maintain the pH.

Calculation of pH of a buffer

The pH of a buffer can be calculated using the Henderson-Hasselbalch equation.

$$pH = pK_a + \log_{10} \frac{[A^-]}{[HA]}$$

$[A^-]$ is the concentration of the anion, which is assumed to be the same as the concentration of the salt, as it fully dissociates in solution.
$[HA]$ is the concentration of the acid.

Example: If the K_a for ethanoic acid at 25°C is 1.8×10^{-5} mol dm^{-3} what is the pH of a solution which contains 1.0 mol dm^{-3} sodium ethanoate and 0.1 mol dm^{-3} ethanoic acid?

$$pH = pK_a + \log_{10} \frac{[A^-]}{[HA]}$$

$$pH = -\log_{10}K_a + \log_{10} \frac{[A^-]}{[HA]}$$

$pH = -\log_{10}(1.8 \times 10^{-5}) + \log (1.0/0.1)$
$pH = 4.7 + 1 = 5.7$

Salt hydrolysis

A salt solution may be acid, neutral or alkaline depending on the nature of the interaction of the salt ions with water (salt hydrolysis). The cations and anions of the dissociated salt accept hydrogen ions from water or donate hydrogen ions to water.

Type of salt	Acid, alkaline or neutral	example
Salt made from a strong acid and a strong base	neutral	Sodium chloride, Potassium sulfate
Salt made from a weak acid and a strong base	Alkaline – the negative ion reacts with water, the water donates a proton to the negative ion, leaving OH^- ions in solution $$A^- + H_2O \rightleftharpoons HA + OH^-$$	Sodium ethanoate
Salt made from a weak base and strong acid	Acidic – the positive ion reacts with water, donating a proton to form acidic H_3O^+ $$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$	Ammonium chloride
Salt made from a weak acid and a weak base	Acidic or alkaline depending on the strength of the acid or alkali.	Ammonium ethanoate

? Revision Questions

1 1. Which one of the following solutions has a pH of 1?

A   0.1 mol dm^{-3} HCl

B   0.1 mol dm^{-3} H$_2$SO$_4$

C   0.2 mol dm^{-3} HCl

D   0.2 mol dm^{-3} H$_2$SO$_4$

2 Which one of the following salts would produce a neutral solution when dissolved in water?

A   ammonium chloride

B   potassium chloride

C   potassium ethanoate

D   sodium carbonate

3 3. Which one of the following is the conjugate acid of the hydrogenphosphate(V) ion, HPO$_4^{2-}$?

A   H$_3$PO$_4$

B   H$_3$PO$_4^-$

C   H$_2$PO$_4^-$

D   PO$_4^{3-}$

4
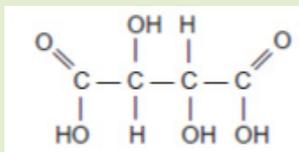
tartaric acid

a) The first pK$_a$ value for the ionisation of tartaric acid is 2.9. Calculate the pH of a 0.1 mol dm^{-3} solution of tartaric acid. Assume only one H$^+$ dissociates.

[3]

b) If tarataric acid is titrated with NaOH state a suitable inducator, and explain why it is a suitable indictor.

....

.... [2]

c) A mixture of tartaric acid and tartrate ions acts as a buffer solution. Using $C_4H_6O_6$ to represent tartaric acid and $C_4H_5O_6^-$ to represent a tartrate ion, write equations to show how this buffer solution responds to the addition of acid and base.
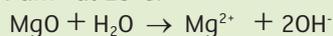
....

.... [2]

5 Explain the mode of action of a buffer of sodium ethanoate and ethanoic acid. You must use equations to explain how it reacts with H^+ and OH^-.

....

....

....

.... [3]

6 Calculate the pH of the solution produced when 0.0006 g of MgO is dissolved in 100 cm^3 of water at 25^{0}C. K_w =1.00 x 10^{-14} mol^{2}dm^{-6} at 25^{0}C.

$$MgO + H_2O \rightarrow Mg^{2+} + 2OH^-$$

[3]

7 Which is the pH of a solution formed when 500 cm^3 of 0.4 mol dm^{-3} HCl is mixed with 500 cm^3 of 0.1 mol dm^{-3} NaOH?

A	13.18
B	12.47
C	0.82
D	0.52