

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

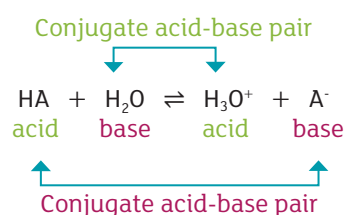
A Brønsted base is a proton acceptor

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

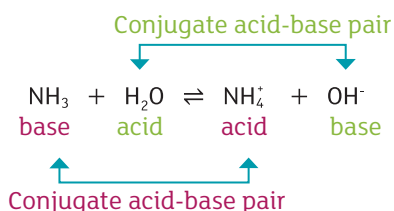
In the forward reaction HA donates a proton to the water molecule, acting as an acid and forming A^- . In the reverse reaction A^- accepts a proton from H_3O^+ and acts as a base. A^- is the conjugate base of the acid HA. The water accepts a proton and acts as a base.



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:



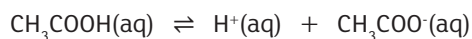
A strong acid is one which fully dissociates into ions in solution.



A full arrow shows that the dissociation is complete. Hydrochloric acid is described as a strong monobasic acid as one mole of HCl produces one mole of $\text{H}^+(\text{aq})$.

A monobasic acid donates one proton per molecule

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

**pH**

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

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

To calculate the hydrogen ion concentration from the pH use

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

Calculation of pH for strong acids

Example 1: What is the pH of $0.02 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$?

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



$$\text{Ratio } 1 \text{ H}_2\text{SO}_4 : 2\text{H}^+ \\ 0.02 : 0.04$$

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

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

$$[\text{H}^+] = 10^{(-\text{pH})} \\ [\text{H}^+] = 10^{(-1.0)} = 0.1 \text{ mol dm}^{-3} \\ \text{H}_2\text{SO}_4 \rightarrow 2\text{H}^+ + \text{SO}_4^{2-} \\ 1 \text{ mol} : 2 \text{ mol H}^+ \\ [\text{H}_2\text{SO}_4] = 0.1/2 = 0.05 \text{ mol dm}^{-3}$$

The ionic product of water K_w

Water partially dissociates into hydrogen ions and hydroxide ions



K_w is the ionic product of water

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

At 25°C , $K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$
The units of K_w are always $\text{mol}^2 \text{ dm}^{-6}$

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

Also

$$\text{p}K_w = -\log_{10}K_w = 14 \text{ at } 25^\circ\text{C}$$

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 $[\text{H}^+] = [\text{OH}^-]$ because
 $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$

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

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.
 $K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ at 298 K

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

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

$$[H^+] = 1 \times 10^{-13} \text{ mol dm}^{-3}$$

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

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 $\text{p}K_a$ values. If K_a is large then $\text{p}K_a$ is small and the acid is strong.

$$\text{p}K_a = -\log_{10}K_a$$

Example

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

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

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

ethanoic acid at this temperature?

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

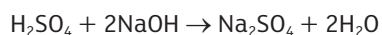
$$[H^+] = 1.34 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log_{10}(1.34 \times 10^{-3}) = 2.87$$

Calculating pH after neutralisation

Example: Calculate the pH of a solution resulting from mixing 25 cm³ of 0.1 mol dm⁻³ sulfuric acid and 25 cm³ 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.



$$\text{Moles of NaOH} = \frac{V \times C}{1000} = \frac{25 \times 0.1}{1000} = 0.0025$$

$$\text{Moles of H}_2\text{SO}_4 = \frac{V \times C}{1000} = \frac{25 \times 0.1}{1000} = 0.0025$$

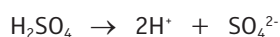
Ratio is 2NaOH : 1H₂SO₄

So 0.0025 mol of NaOH reacts with 0.00125 mol of H₂SO₄

The sulfuric acid is in excess by 0.0025 - 0.00125 = 0.00125 moles

The 0.00125 moles is dissolved in 50 cm³ (25+25) of solution.

This is a concentration of 0.025 mol dm⁻³



$$\begin{array}{lcl} \text{Ratio 1 H}_2\text{SO}_4 & : & 2\text{H}^+ \\ 0.025 & : & 0.050 \end{array}$$

$$\text{pH} = -\log_{10}[\text{H}^+] = -\log_{10}(0.050) = 1.3$$

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 cm³ 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 cm³ 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 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 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

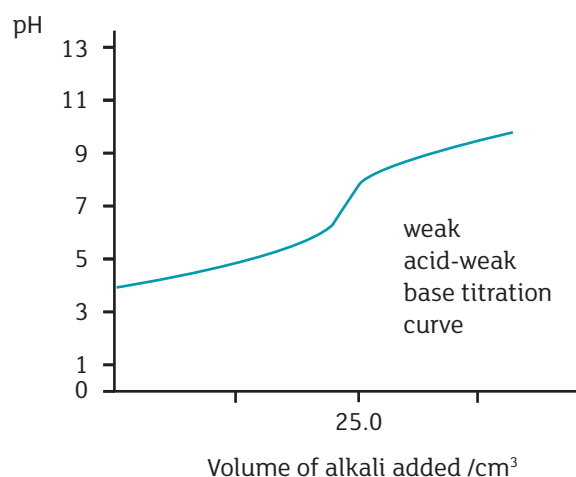
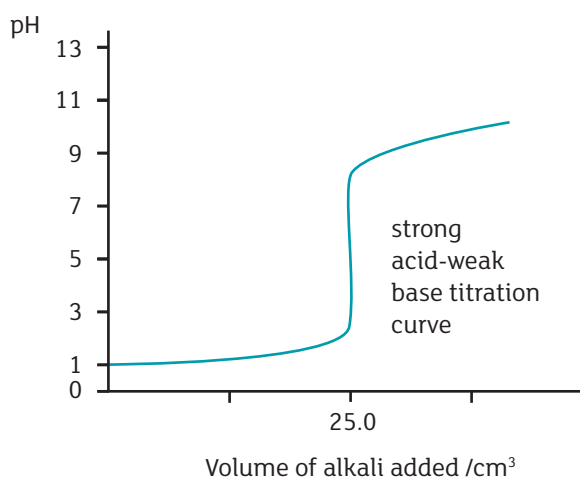
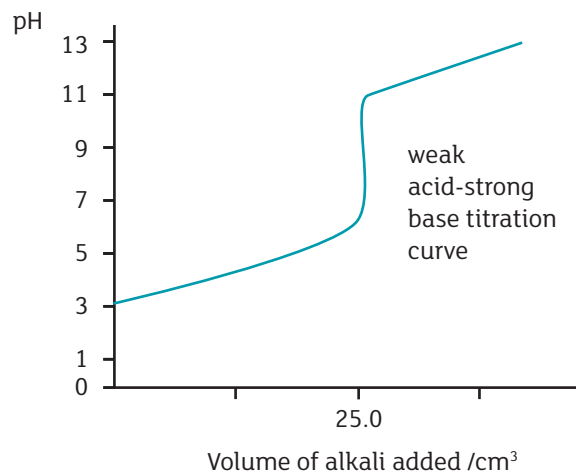
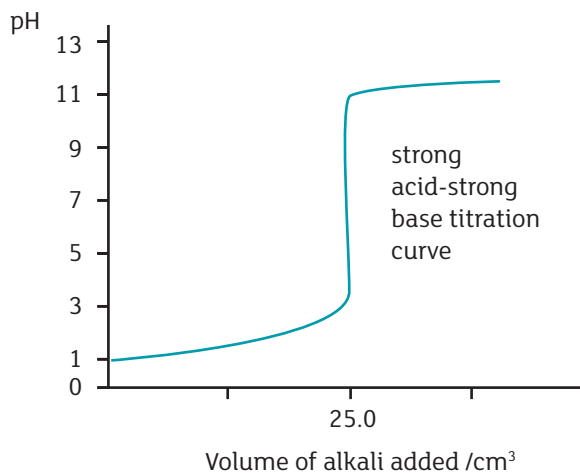
If the base is added to the acid in the conical, the curve starts at pH 3 (weak acid) and there is a very gradual increase, until at the endpoint the pH changes rapidly from 6 to 10 and there is a vertical part on the curve. The curve ends at pH 13 approx (strong alkali). Any indicator which changes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

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

If the base is added to the acid 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



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 ethanoate is a buffer.

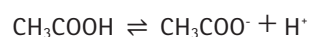
How a buffer solution works.

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.

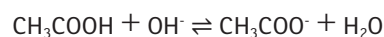
Adding acid (H⁺) to a buffer



- 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



- 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 $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$ 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.

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

[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?

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

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

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

$$\text{pH} = 4.7 + 1 = 5.7$$

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 $\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$ | 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 ₃ O ⁺ $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$ | 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. Which one of the following solutions has a pH of 1?

- A 0.1 mol dm⁻³ HCl
- B 0.1 mol dm⁻³ H₂SO₄
- C 0.2 mol dm⁻³ HCl
- D 0.2 mol dm⁻³ H₂SO₄

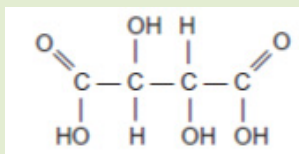
2. Which one of the following salts would produce a neutral solution when dissolved in water?

- A ammonium chloride
- B potassium chloride
- C potassium ethanoate
- D sodium carbonate

3. Which one of the following is the conjugate acid of the hydrogenphosphate(V) ion, HPO₄²⁻?

- A H₃PO₄
- B H₃PO₄⁻
- C H₂PO₄⁻
- D PO₄³⁻

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 tartaric acid is titrated with NaOH state a suitable indicator, and explain why it is a suitable indicator.

.....
 [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.

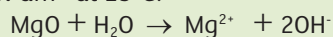
.....
 [2]

- 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 cm³ of water at 25°C. $K_w = 1.00 \times 10^{-14} \text{ mol}^2\text{dm}^{-6}$ at 25°C.



.....
 [3]

- 6 Which is the pH of a solution formed when 500 cm³ of 0.4 mol dm⁻³ HCl is mixed with 500 cm³ of 0.1 mol dm⁻³ NaOH?

- A 13.18
 B 12.47
 C 0.82
 D 0.52

