

WJEC Chemistry A-level

3.9: Acid-Base Equilibria

Detailed Notes

Welsh Specification

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Lowry-Brønsted Theory

Acid-base equilibria involve the **transfer of protons** between substances. Therefore, substances can be classified as **acids or bases** depending on their interaction with protons. This is the **Lowry-Brønsted theory** that helps to classify substances.

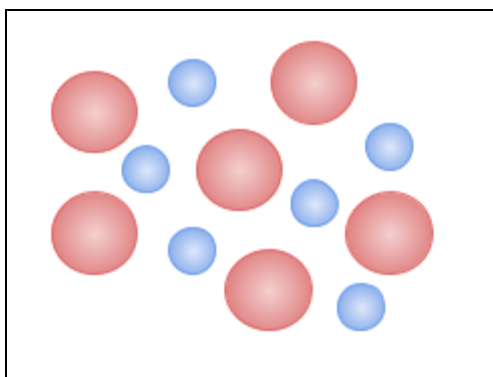
A Lowry-Brønsted **acid** is a proton **donor**. For example, ammonium ions (NH_4^+).

A Lowry-Brønsted **base** is a proton **acceptor**. For example, hydroxide ions (OH^-).

Acid and Base Strength

Acid strength doesn't refer to the concentration of a solution. A **strong acid** is defined as being:

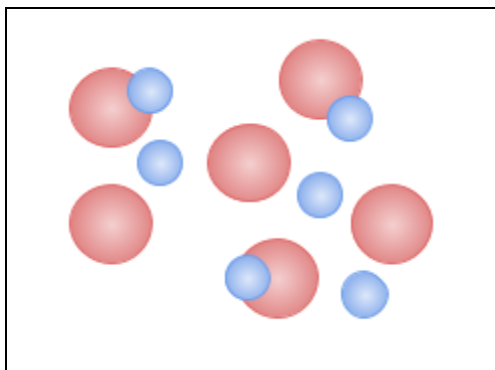
An acid that (almost) completely dissociates into its ions.



Examples of strong acids include HCl , H_2SO_4 and HNO_3 . The **pH** of strong acids ranges from 0 to 3.

In comparison, a **weak acid** is defined as being:

An acid that partially dissociates when in solution.





Examples of weak acids include any organic carboxylic acid - like ethanoic acid. The **pH** of weak acids ranges from 4 to just below 7.

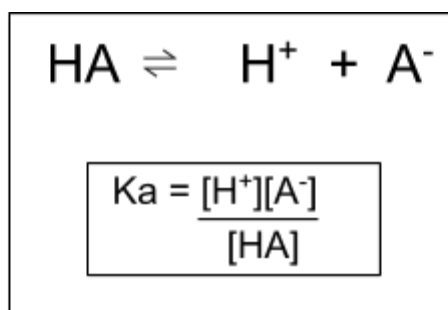
The same definitions are true for **strong and weak bases**.

Examples of **strong bases** are NaOH, KOH and Ca(OH)₂. Strong bases have **pH** 12-14.

Examples of **weak bases** are NH₃ and CH₃NH₂. Weak bases have **pH** from just above 7 to 11.

Dissociation Constant Ka

Due to weak acids and bases only being able to **slightly dissociate**, they form an **equilibrium system** with an equilibrium dissociation constant, **Ka**.



The **stronger** the acid, the **higher** the Ka value. This is because strong acids **dissociate** to ions more, meaning the **concentration of ions** at equilibrium is much greater, making Ka increase in value.

For a **weak acid** you can assume that all the H⁺ ions in solution come from the acid so that [H⁺_(aq)] ≈ [A⁻_(aq)] and you can assume that [HA]_{equilibrium} ≈ [HA]_{start}.

So for a weak acid:

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

Ka has the **units** mol dm⁻³.

Ka can also be used to find **pKa**:

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

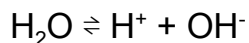
$$K_a = 10^{-\text{pKa}}$$





The Ionic Product of Water

In **water** the following **equilibrium** is set up:



So,

$$K_c = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

Since **[H₂O]** is very **large** compared to [H⁺] and [OH⁻], **[H₂O]K_c** can be considered to be **constant**. Then [H₂O]K_c = K_w and so K_w = [H⁺][OH⁻]:

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

At **25°C**, room temperature, K_w has a **constant value of 1 x 10⁻¹⁴**. However, as temperature changes, the value of this constant changes.

The **forward reaction** in the equilibrium of water is **endothermic** and is therefore favoured when the temperature of the water is increased. As a result, the pH at which water is neutral (concentration of H⁺ and OH⁻ is still the same) **decreases with rising temperature**.

Acid-Base Calculations

The relationships between **K_a**, **pK_a**, **K_w** and **[H⁺]** can be used to carry out calculations involving weak or strong acids and bases.

Depending on the reaction taking place and the relative concentrations of the species, a different method has to be used:

Strong acid - Assume [H⁺] is equal to [HA]. Use this in the formula $\text{pH} = -\log_{10}[\text{H}^+]$.

Strong base - Use K_w to find [H⁺] then use the formula $\text{pH} = -\log_{10}[\text{H}^+]$.

Weak acids - Use K_a. Assume [H⁺] and [A⁻] are the same for monoprotic acids. Assume [HA] at equilibrium is the same as the concentration of weak acid at the start.

Buffers - Use K_a, but remember: [H⁺] ≠ [A⁻]

If [HA] = [A⁻] - In this case, pK_a is equal to pH, so find pK_a.

Titration Curves

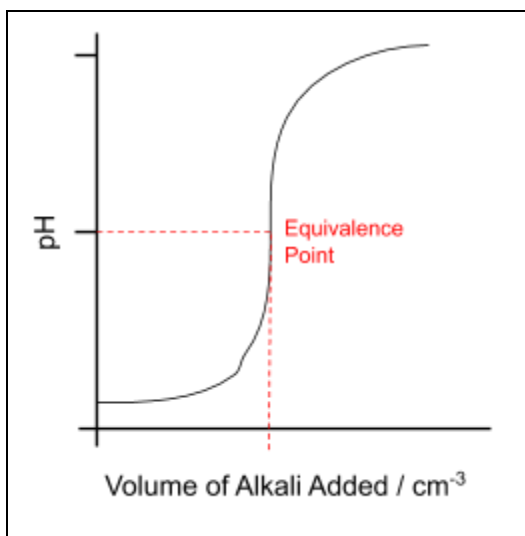
A pH titration curve shows how **pH of a solution changes** during an acid-base reaction. When the species reacts, a **neutralisation point** is reached which can be identified as a **large**





vertical section on the pH curve. The neutralisation point is also known as the **equivalence point**.

To produce a pH curve, an alkali is slowly added to an acid (or vice versa) and the pH measured at **regular intervals** using a **pH probe**. The **smaller** the added volumes, the **more accurate** the curve produced.



For a **strong acid - strong base** reaction, this **neutralisation** point occurs around **pH 7**. Other combinations of strong and weak acids and bases results at a **different neutralisation point**:

Strong Acid + Strong Base = pH 7

Strong Acid + Weak Base < pH 7 (more acidic)

Weak Acid + Strong Base > pH 7 (more basic)

Weak Acid + Weak Base = normally pH 7 but hard to determine

Buffer Action

An **acidic buffer solution** is formed from a weak **acid and one of its salts** and a **basic buffer solution** is formed from a weak **base and one of its salts**. This produces a mixture containing **H⁺ ions** and a large **reservoir of OH⁻ ions** which helps to **resist any change** in pH. Therefore, a buffer solution is defined as:

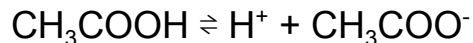
A solution which is able to resist changes in pH when small volumes of acid or base are added.





The large reservoir of OH⁻ ions allows the ratio of acid to base in the mixture to be kept **almost constant**.

The following **equilibrium** is set up within the **acidic buffer** solution made by mixing **sodium ethanoate with ethanoic acid**:



If a small amount of **acid is added**, the concentration of **H⁺ increases**. Most of the extra H⁺ ions combine with **CH₃COO⁻** ions to form **CH₃COOH** so the **equilibrium shifts to the left**. This reduces the concentration of H⁺ to near to its **original value** so the pH does not change. This is how a buffer solution works.

Buffer Calculations

K_a, **pK_a**, **pH** and **K_w** can all be used in buffer calculations. These are long, often complex, problems that use acid-base relationships. There are two main types, with differing methods:

- Acid + Base**
- Find the number of **moles** of each species after they have reacted.
 - Calculate the **concentration** at equilibrium using the **total volume**.
 - Use **K_a** to find [H⁺] and then use $\text{pH} = -\log_{10}[\text{H}^+]$.

- Acid + Salt**
- Find the **moles** of the salt and the acid.
 - Use **K_a** to find pH.

Example:

Q) A buffer solution contains 0.35 mol dm⁻³ methanoic acid and 0.73 mol dm⁻³ sodium methanoate. For methanoic acid, $K_a = 1.6 \times 10^{-4}$ mol dm⁻³. Find the pH of this buffer solution.

A) First write out the equation of the reaction:



Next find the expression for K_a :

$$K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$$

Rearrange K_a to give [H⁺]:

$$[\text{H}^+] = K_a \times \frac{[\text{HCOOH}]}{[\text{HCOO}^-]}$$

Substitute in the values given:

$$[\text{H}^+] = (1.6 \times 10^{-4}) \times (0.35 / 0.73) = 7.67 \times 10^{-5} \text{ mol dm}^{-3}$$

Convert [H⁺] to pH:

$$\text{pH} = -\log_{10}[\text{H}^+] = -\log_{10}(7.67 \times 10^{-5}) = 4.12$$

Uses of Buffers

Buffer solutions are **common in nature** in order to keep systems regulated. This is important as **enzymes** or reactions in living organisms often require a **specific pH**, which can be maintained using a **buffer solution**.

Industrial processes now also use buffer solutions to try and maintain the **optimum** reaction conditions for large scale manufacturing.





Chemical Indicators

Specific indicators have to be used for specific reactions as they can only **indicate a pH change within a certain range**.

The two most common indicators used at A-Level are **methyl orange** and **phenolphthalein**:

Methyl Orange

Methyl orange is used in reactions with a more **acidic neutralisation** point.

The colour change occurs at **pH range 3.1-4.4**. It is **red** in acids and turns **yellow** at the neutralisation point.

Phenolphthalein

Phenolphthalein is used for reaction with a more **basic neutralisation** point. The colour change occurs at **pH range 8.3-10**. It is **pink** in alkalis and turns **colourless** at the neutralisation point.

It is really important that the **correct indicator** is selected to use in a titration depending on the chemicals being used and the order in which they are being combined.

