Edexcel IAL Chemistry A-level

Topic 14: Acid-base Equilibria

Detailed notes

Brønsted-Lowry Acids and Bases

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.

A Brønsted-Lowry **acid** is a **proton donor**. For example, ammonium ions (NH_4^+).
A Brønsted-Lowry **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 completely dissociates to ions when in solution, with pH 0-1.

Example:

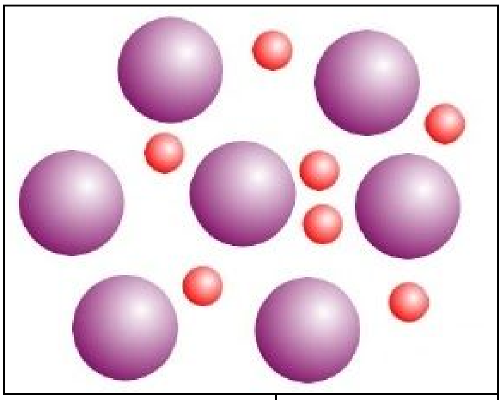
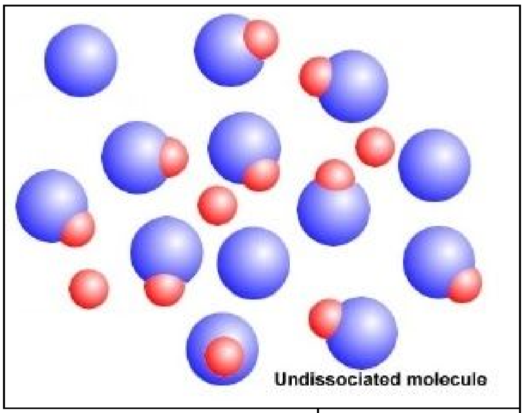


Image courtesy of Socratic

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

An acid that only slightly dissociates when in solution, with pH between 3 and 7.

Example:



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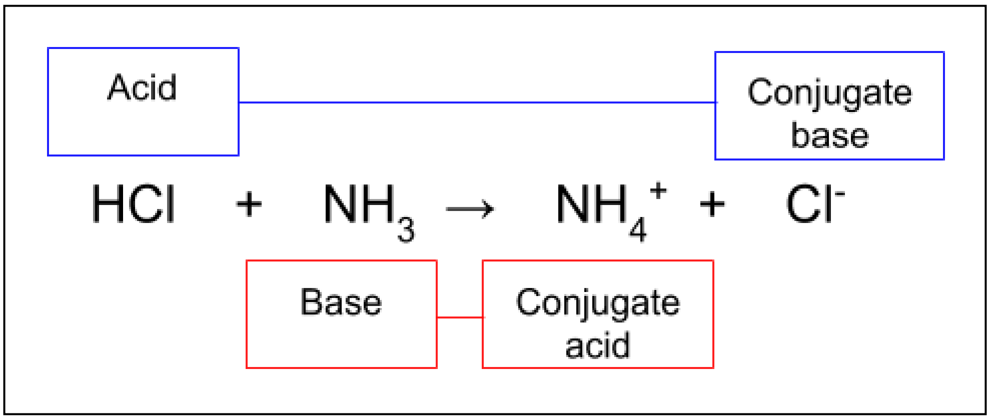
The same definitions are true for **strong** and **weak bases**. Strong bases have pH between 12-14 and weak bases have pH between 7-11.

Brønsted–Lowry conjugate acid-base pairs

A **conjugate acid** is the species formed when a **base accepts a proton**. A **conjugate base** is the species formed when an **acid donates a proton**. These form conjugate acid-base pairs.

Example:



$$HCl + NH_3 \rightarrow NH_4^+ + Cl^-$$

Determining pH

pH is a measure of **acidity and alkalinity**. It is a **logarithmic** scale from 0 to 14, giving the concentration of **H^+ ions** in a solution. 0 is an **acidic** solution with a high concentration of H^+ ions whereas 14 is a **basic** solution with a low concentration of H^+ ions. pH can be calculated using the concentration of hydrogen ions, $[H^+]$, as follows:

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

This equation also allows the concentration of H^+ ions to be determined if the pH is known. When using these equations, the concentration of H^+ ions is given in **mol dm^{-3}**.

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

The concentration of H^+ ions is equivalent to the **concentration of a strong acid,** as it **completely dissociates** to ions in solution.

Weak Acids and Bases

Weak acids and bases only **slightly dissociate** in solution, forming an **equilibrium** mixture. Therefore, the reaction has an equilibrium dissociation constant, **K_a**.

$$HA \rightleftharpoons H^+ + A^-$$

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

In a similar way to $[H^+]$, constant Ka can be found using **pKa**:

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

$$K_a = 10^{-pK_a}$$

The value pKa is a logarithmic acid dissociation constant, representing how acidic something is. A **low value** indicates a **strong acid**.

These relationships of Ka, pKa and $[H^+]$ can be used to find the **pH of weak acids and bases**. Depending on the reaction and the relative concentrations, a different method may have to be used:

HA in excess - Use [HA] and $[A^-]$ along with Ka to find $[H^+]$, then pH.

A^- in excess - Use Kw to find $[H^+]$, then pH.

$HA = A^-$ - In this case, pKa is equal to pH, therefore find pKa.

Diluting Acids

If you dilute a strong acid **10 times** its pH will increase by **one unit**, because pH is a **logarithmic scale**. Diluting it **100 times** and **1000 times** would therefore increase the pH by **two units** and **three units,** respectively.

Weak acids do not behave in the same way. Weak acids are **not fully dissociated in solution**, so diluting them causes the **equilibrium** to **shift** to oppose the change. This means a **10x dilution** of a weak acid would increase the pH by **less than one unit**.

Calculating the Ka of weak acids

Weak acids only **partially dissociate** in solution. Therefore, the **equilibrium** of a weak acid has to be taken into account.

1. The initial concentrations, change in concentrations and equilibrium concentrations of the reactants and products have to be found.

2. The concentration of H^+ ions can then be found using the pH given.
3. This value can be used to find the actual equilibrium concentrations.
4. Finally, these values can be substituted into the expression for Ka.

Example

A weak acid, HA, with a concentration of 0.25 M has a pH of 3.5. What is its Ka?

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

We assume that ‘x’ mol of HA dissociates to A^- and H_3O^+.

	HA	**A^-**	**H_3O^+**
Initial	0.25	0	0
Change	-x	+x	+x
End	0.25 - x	x	x

Using the pH value give, the $[H^+]$ (= x) can be calculated:

$$[H_3O^+] = [H^+] = 10^{-pH}$$

$$[H^+] = 10^{-3.5} = 3.16 \times 10^{-4}\ M$$

$$x = 3.16 \times 10^{-4}\ M$$

Substituting into the expression for Ka and using the equilibrium concentrations:

$$Ka = \frac{[H^+][A^-]}{[HA]} = \frac{(x)(x)}{(0.25-x)}$$

We can now substitute in the value of x calculated earlier: $x = 3.16 \times 10^{-4}$ M

$$Ka = \frac{(3.16 \times 10^{-4})^2}{(0.25 - (3.16 \times 10^{-4}))}$$

$$Ka = 3.99 \times 10^{-7}$$

Ionic Product of Water

Water **slightly dissociates** to form hydroxide and hydrogen ions as an equilibrium with its own equilibrium constant, **Kw**.

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

At **25°C**, room temperature, Kw has a constant value of **1.0×10^{-14}**. However, as temperature changes, **this value 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, as temperature increases, **more H^+ ions** are produced meaning the water becomes **more acidic.**

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

In the same way that pKa can be calculated from Ka, **pKw** can be calculated from **Kw**.

$$pK_w = -\log_{10}K_w$$

$$K_w = 10^{-pK_w}$$

The pH of a strong base can be calculated using pKw or Kw. For a **strong base**, the concentration of OH^- will be the **same** as the concentration of the base.

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

Rearrange Kw to find $[H^+]$: $[H^+] = \dfrac{Kw}{[OH^-]}$

Use $Kw = 10^{-14}$ and the concentration of the base to find $[H^+]$.

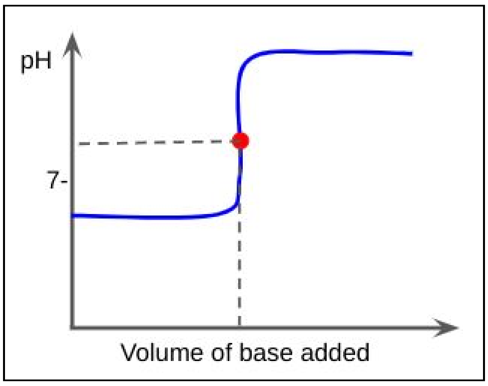
Finally, calculate pH using: $pH = -\log_{10}[H^+]$

Titration Curves

A pH titration curve shows how pH of a solution **changes** during an **acid-base reaction**. When an acid and base react, a **neutralisation point** is reached, identified as a large **vertical section** of the graph the pH titration curve.

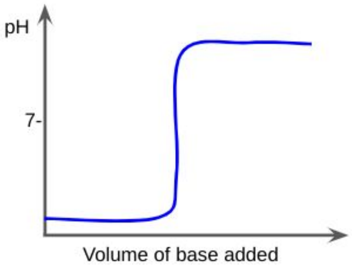
To obtain a pH titration curve, alkali is slowly added to an acid (or vice versa) and the pH is regularly measured with a **pH probe.** The **smaller** the added volumes, the **more accurate** the curve produced.

Example: The red dot indicates the equivalence point

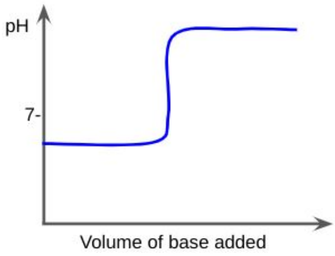


For a strong acid - strong base reaction, this neutralisation point occurs around **pH 7**. Other combinations of strong and weak acids and bases results in a **different neutralisation point**:

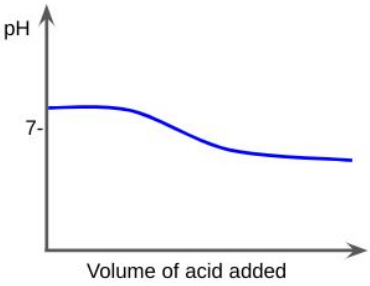
- Strong Acid + Strong Base = pH 7



- 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

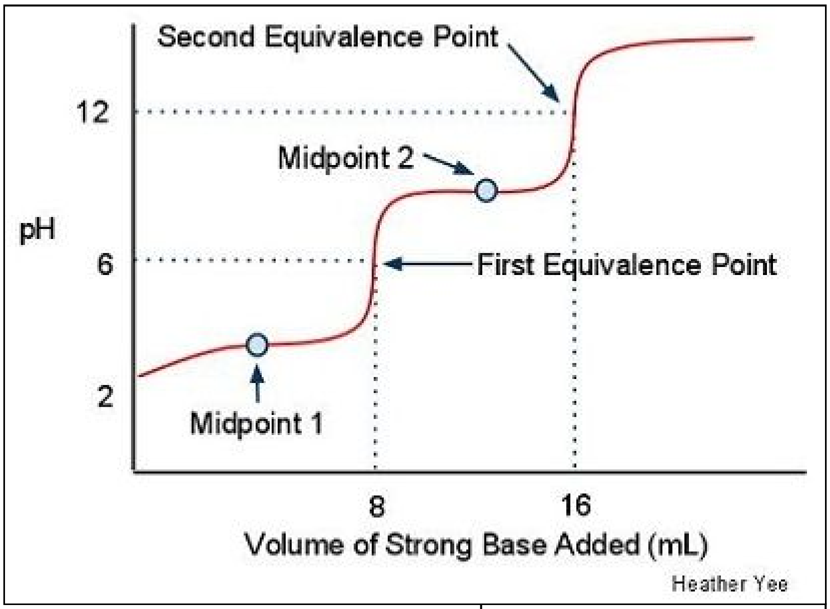


Polyprotic Acids and Bases

Polyprotic acids can donate **more than one proton**, compared to **monoprotic** acids which can only donate one. For example, phosphoric acid, H_3PO_4, is a triprotic acid as it can donate three protons.

Titrations involving polyprotic acids create different shaped curves. They have more than one vertical region corresponding to **more than one equivalence point**.

Example: ***Strong base added to a strong diprotic acid***



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Calculating Ka from Titration Curve

The vertical region of a titration curve is the **equivalence point**. At **half-equivalence point** (when half the volume of acid/base at the equivalence point is added) the **pH is equal to pKa**, by definition.

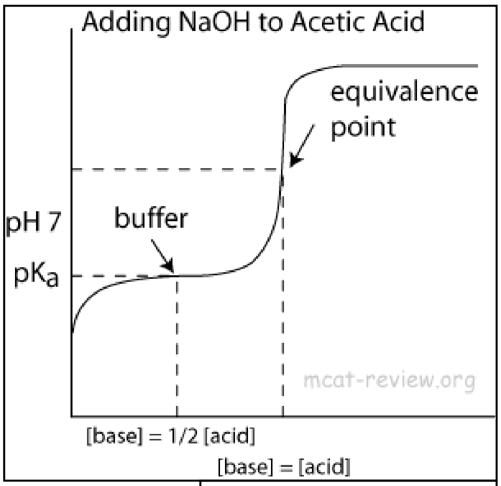


Image courtesy of stack exchange

Therefore, by reading the pH at half the equivalence point, Ka can be easily calculated from pKa.

Indicators

Specific chemical 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 - used for reactions with a **more acidic** neutralisation point.
- red in acids and turns **yellow** at the neutralisation point.

Phenolphthalein - used for reaction with a slightly **more basic** neutralisation point.
- pink in alkalis and turns **colourless** at the neutralisation point.

Indicator	**pH at colour change**	**Colour in acid**	**Colour in base**
Methyl orange	3-5	**Red**	**Yellow**
Phenolphthalein	8-10	**Colourless**	**Pink**
Litmus	5-8	**Red**	**Blue**

It is important that, depending on the strength of the titration reactants, the **correct indicator is selected** so that the colour change occurs at neutralisation.

Buffer Action

A buffer solution is formed from a **weak acid and its salt** or a **weak acid and a base**. 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**.

Consider the following buffer solution:

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

The **OH^- concentration** will **increase** if a small amount of base is added, making the solution more basic. The extra OH^- ions will react with the NH_4^+ ions, to form the **original reactants**. Therefore, the equilibrium will shift to the left to remove the OH^- ions and stop the pH from changing largely.

Buffer Calculations

These are long calculations that use acid-base calculations. There are two types:

Acid + Base - Find the number of moles of each species.
- Calculate their concentration when at equilibrium using the total volume.
- Use Ka to find [H^+], and therefore pH.

Acid + Salt - Find the moles of the salt.
- Use Ka to find pH.

Example: A buffer solution contains 0.35 mol dm^{-3} methanoic acid and 0.67 mol dm^{-3} sodium methanoate. For methanoic acid, Ka = 1.6 x 10^{-4} mol dm^{-3}. Find the pH of this buffer.

We **assume** that the **sodium methanoate completely dissociates** so that the equilibrium concentration of $HCOO^-$ is the same as the initial concentration of $HCOO^-Na^+$. Similarly, HCOOH only slightly dissociates so we assume that the **equilibrium concentration** is equal to the **initial concentration**.

1. First find the expression for Ka for methanoic acid

$$HCOOH \rightleftharpoons H^+ + HCOO^-$$

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

2. Rearrange the expression to find [H^+]

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

$$[H^+] = 1.6 \times 10^{-4} \times (0.35/0.67) = 8.4 \times 10^{-5}$$

3. Convert [H^+] to pH

$$pH = -\log_{10}(8.4 \times 10^{-5}) = 4.08$$

Adding small volumes

The pH of a buffer solution doesn't change much but will change in the **order of 0.1 or 0.01 units of pH** when a **small volume** of acid or base is added.

Adding small amounts of **acid (H^+) increases the concentration** of the acid in the buffer solution meaning the overall solution will get slightly **more acidic**.

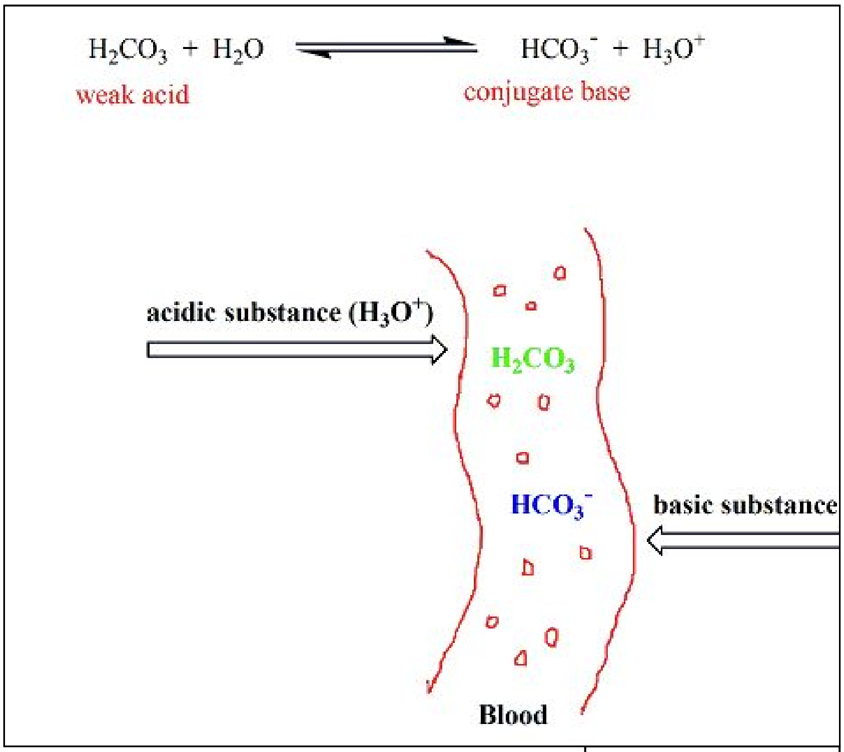
Adding small amounts of **base (OH^-) decreases the concentration** of acid in the buffer solution meaning the overall solution will get slightly more **basic**.

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. Buffers can be used to prevent the deterioration of food when fungus or bacteria may otherwise cause pH changes.

Another important buffer in nature is found in the human circulatory system. The **pH of human blood** is maintained in a buffer between **carbonic acid and bicarbonate ions**. These ions **neutralise any acidic substances** that enter the bloodstream, converting them to carbonic acid and water.

Example:



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