1C Acid and buffers

The road to acids

- The definition of acids and bases have changed over time.
- At AS we looked at the definition of acid base behaviour as defined by Bronsted - Lowrey in 1923.
- They defined:

Acids - proton donors

Base - proton acceptors

Alkali - a base that dissolves in water forming OH^- ions

The role of H^+ in reactions of acids

- A **hydrogen ion** is just a hydrogen **atom** that has l**ost an electron**.
- As hydrogen only has 1 electron this means that a hydrogen ion is just a proton.
- **H^+** and **proton** mean the same.
- In **water** the acid **dissociates** producing **hydrogen ions / protons:**

$$HCl_{(g)} + aq \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

$$H_2SO_{4(l)} + aq \rightarrow H^+_{(aq)} + HSO_4^-{}_{(aq)}$$

Mono, di and tri - basic acids:

- Acids are categorised on the number of acidic hydrogen's / protons they can release:

Monobasic: releases 1 proton

$$HCl_{(aq)} + aq \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

Dibasic: releases 2 protons

$$H_2SO_{4(aq)} + aq \rightarrow H^+_{(aq)} + HSO_4^-{}_{(aq)}$$

$$HSO_4^-{}_{(aq)} + aq \leftrightarrows H^+_{(aq)} + SO_4^{2-}{}_{(aq)}$$

Tribasic: releases 3 protons

$$H_3PO_{4(aq)} + aq \leftrightarrows H^+_{(aq)} + H_2PO_4^-{}_{(aq)}$$

$$H_2PO_4^-{}_{(aq)} + aq \leftrightarrows H^+_{(aq)} + HPO_4^{2-}{}_{(aq)}$$

$$HPO_4^-{}_{(aq)} + aq \leftrightarrows H^+_{(aq)} + PO_4^{3-}{}_{(aq)}$$

Acid - base reactions:

- Acids react with:

Carbonates
Bases (metal oxides)
Alkalis (metal hydroxides)

- In every reaction the acid is neutralised and **water** is formed as part of the reaction.
- Looking at the **ionic** equation we can see why water is formed in each case.
- This means we have to remove the **spectator ions**
- These are species that do not change from reactants to products (including the state symbols).
- It doesn't matter whether the acid is **strong** or **weak** as acids will release more H^+ ions as they are used up in the reaction **LCP**

Carbonates:

Full: $2HCl_{(aq)} + CaCO_{3(s)} \rightarrow CaCl_{2(aq)} + CO2_{(g)} + H_2O_{(l)}$

Ions: $2H^+_{(aq)} + 2Cl^-_{(aq)} + CaCO_{3(s)} \rightarrow Ca^{2+}_{(aq)} + 2Cl^-_{(aq)} + CO2_{(g)} + H_2O_{(l)}$

Ionic: $2H^+_{(aq)} + CaCO_{3(s)} \rightarrow Ca^{2+}_{(aq)} + CO2_{(g)} + H_2O_{(l)}$

- If the carbonate is in solution it simplifies further:

Full: $2HCl_{(aq)} + CaCO_{3(aq)} \rightarrow CaCl_{2(aq)} + CO2_{(g)} + H_2O_{(l)}$

Ions: $2H^+_{(aq)} + 2Cl^-_{(aq)} + Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow Ca^{2+}_{(aq)} + 2Cl^-_{(aq)} + CO2_{(g)} + H_2O_{(l)}$

Ionic: $2H^+_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow CO2_{(g)} + H_2O_{(l)}$

Bases:

Full: $2HNO_{3(aq)} + MgO_{(s)} \rightarrow Mg(NO_3)_{2(aq)} + H_2O_{(l)}$

Ions: $2H^+_{(aq)} + 2NO_3^-{}_{(aq)} + MgO_{(s)} \rightarrow Mg^{2+}_{(aq)} + 2NO_3^-{}_{(aq)} + H_2O_{(l)}$

Ionic: $2H^+_{(aq)} + MgO_{(s)} \rightarrow Mg^{2+}_{(aq)} + H_2O_{(l)}$

Alkalis:

Full: $H_2SO_{4(aq)} + 2KOH_{(aq)} \rightarrow K_2SO_{4(aq)} + 2H_2O_{(l)}$

Ions: $2H^+_{(aq)} + SO_4^{2-}{}_{(aq)} + 2K^+_{(aq)} + 2OH^-_{(aq)} \rightarrow 2K^+_{(aq)} + SO_4^{2-}{}_{(aq)} + 2H_2O_{(l)}$

Ionic: $\cancel{2}H^+_{(aq)} + \cancel{2}OH^-_{(aq)} \rightarrow \cancel{2}H_2O_{(l)}$

Redox reactions of acids with metals:

- These are **not acid base reactions** as water is not made, they are just **REDOX** reactions:

Full: $2HCl_{(aq)} + Mg_{(s)} \rightarrow MgCl_{2(aq)} + H_{2(g)}$

Ions: $2H^+_{(aq)} + 2Cl^-_{(aq)} + Mg_{(s)} \rightarrow Mg^{2+}_{(aq)} + 2Cl^-_{(aq)} + H_{2(g)}$

Ionic: $2H^+_{(aq)} + Mg_{(s)} \rightarrow Mg^{2+}_{(aq)} + H_{2(g)}$

- These type of reactions are acids behaving as strong oxidising agents.
- Conc. nitric and sulphuric acids are examples of these types of reactions.

Conjugate acid - base pairs

Acids as proton donors:

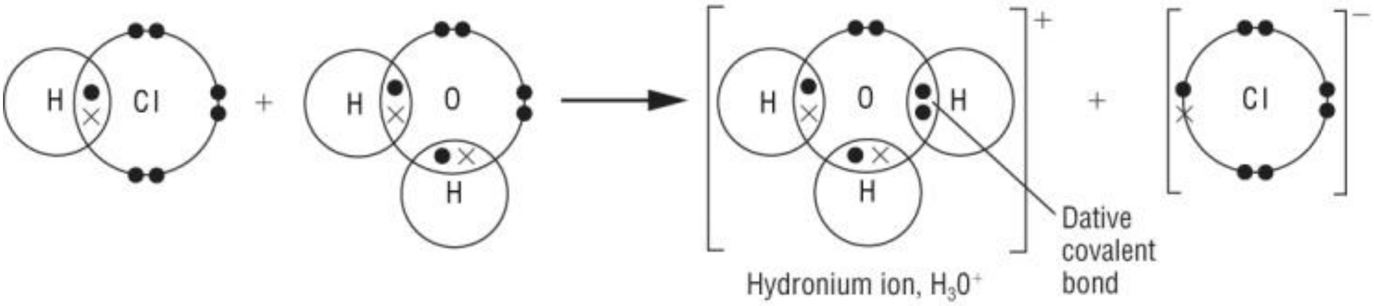
- Acids are molecules that contain hydrogen that can be released as **H^+**
- This will only donate protons if there is something to accept it - a base

Hydronium ions:

- Aqueous acids donate their protons to water. This makes water a proton acceptor forming the hydronium ion / oxonium ion:

$$\mathbf{HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}}$$

hydronium ion



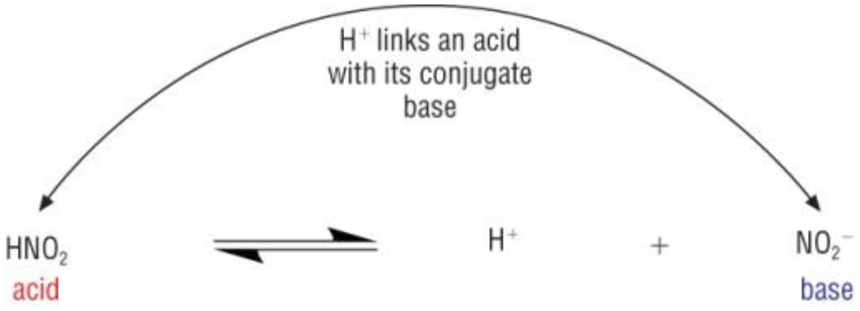
- This reaction is often simplified to:

$$\mathbf{HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}}$$

hydronium ion

- **$H^+_{(aq)}$** is a simplified way of writing **$H_3O^+_{(aq)}$**

Acid - base pairs:



- The forward reaction is when a proton is donated to water forming ions.
- Strong acids fully dissociate meaning products predominate.
- Now consider the reverse reaction.
- The proton is now accepted by the **NO_2^-.**
- This makes this an acid - base pair

Conjugate pairs

- There is a relationship between 2 of the species, one on either side of the equilibrium and they can be considered **conjugate pairs**:

Conjugate pair

$$\underset{\text{acid}}{HNO_{2(aq)}} + \underset{\text{base}}{H_2O_{(l)}} \rightleftarrows \underset{\text{acid}}{H_3O^+_{(aq)}} + \underset{\text{base}}{NO_{2\,(aq)}^-}$$

Congugate pair

- Look at the NO_2 species on both side of the equilibrium. They are in the acid and the base (an acid / base pairpairs.
- Another Conjugate acid / base pair can be seen in the following reaction:

Conjugate pair

$$\underset{\text{base}}{NH_{3(aq)}} + \underset{\text{acid}}{H_2O_{(l)}} \rightleftarrows \underset{\text{base}}{OH^-_{(aq)}} + \underset{\text{acid}}{NH_{4\,(aq)}^+}$$

Congugate pair

<u>What is pH?</u>

The pH scale

- Aqueous acids contain **$[H^+]$** in the range from **10^1 10 10^{-15} Mol dm^{-3}**
- To compress such a large scale we use a **negative logarithmic scale / - logs**
- This reduces the scale to whole numbers and deals with the small concentrations of **$[H^+]$**
- This is the origin of the pH scale which gives us a relationship between pH and the hydrogen concentration:

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

- **OR**

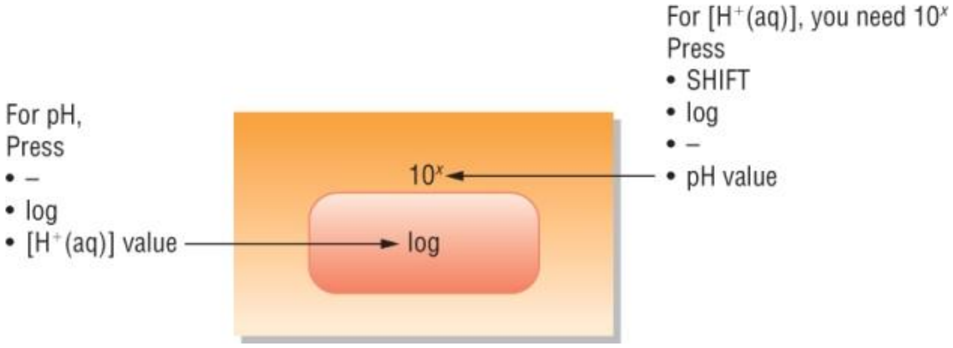
$$[H^+_{(aq)}] = 10^{-pH}$$

What does pH mean:

Low pH	**High $[H^+_{(aq)}]$**
High pH	**Low $[H^+_{(aq)}]$**

Converting between pH and [$H^+_{(aq)}$]

- **[$H^+_{(aq)}$]** and **pH** are not usually whole numbers and may not be in standard form.
- To calculate the pH you will need your calculator:



Calculating the pH of strong acids:

Strong acids – donate protons to water completely
Weak acids – do no donate protons to water very readily (later)

- Consider the following:

$$\mathbf{HCl_{(g)} \xrightarrow{Water} H^+_{(aq)} + Cl^-_{(aq)}}$$

1 mole **1 mole** **1 mole**

- This means that for **strong acids** the **[$H^+_{(aq)}$] = [ACID]**

Examples:

1) Calculate the pH of 1 x 10^{-3} mol dm^3 HCl:

[$HCl_{(aq)}$] = 1 x 10^{-3} mol dm^3

[$H^+_{(aq)}$] = 1 x 10^{-3} mol dm^3

pH = - log [$H^+_{(aq)}$]

pH = - log [1 x 10^{-3}]

pH = 3

2) Calculate the pH of 1 x 10^{-6} mol dm^{-3} HNO_3

[$HCl_{(aq)}$] = 1 x 10^{-6} mol dm^3

[$H^+_{(aq)}$] = 1 x 10^{-6} mol dm^3

pH = - log [$H^+_{(aq)}$]

pH = - log [1 x 10^{-6}]

pH = 6

The ionisation of water

The ionisation of water and K_w

- We always assume that water does not act as an acid or base in reactions.
- Water plays a big part in the understanding of acids.
- In order to understand acids then we need to understand water first:

Water: facts and models

Water conducts electricity. It has a conductivity of 26.6 x 10^{-6} Scm^{-1}

- The fact that water conducts at all means that there must be at least some ions present:

$$H_2O_{(l)} \rightleftarrows H^+_{(aq)} + OH^-_{(aq)}$$

- This means that water would have an equilibrium expression:

$$K_c = \frac{[H^+] \times [OH^-]}{[H_2O]}$$

- Rearrange this to:

$$K_c \times [H_2O] = [H^+] \times [OH^-]$$

- **$[H_2O]$** of water in water is always constant.
- **K_c** is also a constant. These 2 terms can be replaced with one constant which we call
- **K_w** is the **ionic product of water** (basically an kind of equilibrium constant just for water):

$$K_c \times [H_2O] = [H^+] \times [OH^-]$$

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

K_w has an equilibrium constant of 1 x 10^{-14}

PH and the ionic product of water

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

- Where **K_w** is known as the **ionic product of water**.
- At 298K the ionic product of water is 1×10^{-14} $Mol^2\ dm^{-6}$.

$$K_w = [H^+] \times [OH^-] = 1 \times 10^{-14}$$

- The protons and hydroxides are both produced from the dissociation of water.
- This means that the concentrations of both of these ions must be the same (as they both came from water).

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

- This means that in pure water at equilibrium:

$$[H^+] \times [OH^-] = 1 \times 10^{-14}$$
$$[H^+]^2 = 1 \times 10^{-14}$$
$$[H^+] = (1 \times 10^{-14})^{0.5} \quad \text{where } (\ )^{0.5} = \text{square root}$$
$$[H^+] = 1 \times 10^{-7}$$

- The concentration of each of the ions produced by the dissociation of water = **1×10^{-7}** $Mol\ dm^{-3}$
- We know that the **pH of water = 7**
- A **negative logarithmic scale** compresses the values into a smaller range and gives us positive values, more useful to use as comparisons.
- This is the origin of the pH scale which gives us a relationship between pH and the hydrogen concentration:

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

The significance of K_w:

- **K_w** is basically an equilibrium expression linking **$[H^+]$ and $[OH^-]$**.
- We have already seen that at the **pH of water = 7** when the **$[H^+] = [OH^-]$**.

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

Acidic conditions	$[H^+] > [OH^-]$.	**K_w must always equal 1×10^{-14}**
Alkaline conditions	$[H^+] < [OH^-]$.	**$[H^+] \times [OH^-] = 1 \times 10^{-14}$**

The link between $[H^+]$ and $[OH^-]$

- The $[H^+]$ and $[OH^-]$.are linked by the ionic product of water.

$$K_w = [H^+] \times [OH^-] = 1 \times 10^{-14}$$

- A few examples:

pH	1	3	5	7	9	11	13	
$[H^+]$	10^{-1}	10^{-3}	10^{-5}	10^{-7}	10^{-9}	10^{-11}	10^{-13}	
$[OH^-]$	10^{-13}	10^{-11}	10^{-9}	10^{-7}	10^{-5}	10^{-3}	10^{-1}	

- This means it is possible to calculate $[H^+]$ and hence **pH** from $[OH^-]$

pH of strong bases

Strong bases – dissociate completely to generate OH^- ions in water
Weak bases – do not dissociate completely to generate OH^- ions in water (later)

- Consider the following:

$$\begin{array}{ccccc} NaOH_{(s)} & \xrightarrow{\text{Water}} & Na^+_{(aq)} & + & OH^-_{(aq)} \\ \text{1 mole} & & \text{1 mole} & & \text{1 mole} \end{array}$$

- We use the **ionic product of water** to calculate the corresponding $[H^+]$ concentration for bases:

$$K_w = [H^+] \times [OH^-] = 1 \times 10^{-14}$$

Example: 0.1M solution of NaOH

$$\begin{aligned} [H^+] \times [OH^-] &= 1 \times 10^{-14} \\ [H^+] \times 0.1 &= 1 \times 10^{-14} \\ [H^+] &= \frac{1 \times 10^{-14}}{0.1} \\ [H^+] &= 1 \times 10^{-13} \\ pH &= -\log_{10}[H^+_{(aq)}] \\ pH &= -\log_{10}[1 \times 10^{-13}] \\ pH &= 13 \end{aligned}$$

There is a quicker way:

- If you take **$-\log_{10}$ $[OH^-]$** (essentially a '**pOH**') you can use math's of indices to calculate the pH bases on the **ionic product of water, K_w**.
- If you take **$-\log_{10}$** of the **ionic product of water, K_w:**

$$\begin{array}{rcccl} [H^+] & \times & [OH^-] & = & 1 \times 10^{-14} \\ -\log_{10}[H^+] & \times & -\log_{10}[OH^-] & = & -\log_{10}(1 \times 10^{-14}) \\ pH & + & pOH & = & 14 \end{array}$$

Strong and weak acids, calculating the pH for weak acids

Acid - base equilibria:

- Remember, in aqueous solutions acids dissociate.

Strong acids:

- They dissociate fully in water (100%) if they are strong acids:

$$\mathbf{HA_{(aq)} \xrightarrow{Water} H^+_{(aq)} + Cl^-_{(aq)}}$$

Weak acids:

- They partially dissociate in water if they are weak acids:

$$\begin{array}{cccccc} \mathbf{HA_{(aq)}} & \overset{\mathbf{Water}}{\leftrightarrows} & \mathbf{H^+_{(aq)}} & + & \mathbf{Cl^-_{(aq)}} \\ \textbf{1 mole} & & \textbf{0 moles} & & \textbf{0 moles} \\ \textbf{0.99 moles} & & \textbf{0.01 moles} & & \textbf{0.01 moles} \end{array}$$

- This gives us an equilibrium, using ethanoic acid as an example:

$$\begin{array}{cccccc} \mathbf{CH_3COOH_{(l)}} & \overset{\mathbf{Water}}{\leftrightarrows} & \mathbf{H^+_{(aq)}} & + & \mathbf{CH_3COO^-_{(aq)}} \\ \textbf{0.99 moles} & & \textbf{0.01 moles} & & \textbf{0.01 moles} \end{array}$$

- **1 mole** of ethanoic acid dissociates to **0.99 moles** of ethanoic acid forming **0.01 mole** of each of the ions.
- The equilibrium lies well over to the **LHS**
- This means an equilibrium expression can be written:

The acid dissociation constant, K_a

- For ethanoic acid:

$$\mathbf{CH_3COOH_{(l)} \leftrightarrows H^+_{(aq)} + CH_3COO^-_{(aq)}}$$

- An equilibrium expression can be written:

$$K_a = \frac{[H^+] \times [CH_3COO^-]}{[CH_3COOH]}$$

- Notice that we used K_c for **c**oncentrations. We use $\mathbf{K_a}$ when dealing with **a**cids.
- $\mathbf{K_a}$ is known as the **acid dissociation constant** and this can be either calculated or looked up in a table for use in calculations.
- Ethanoic acid has a $K_a = 1.7 \times 10^{-5}$ Mol dm^{-3}.

Units of K_a

- These are worked out in exactly the same way as for K_c:

$$K_a = \frac{[H^+] \times [CH_3COO^-]}{[CH_3COOH]}$$

$$K_a = \frac{\mathrm{mol\,dm^{-3}} \times \mathrm{mol\,dm^{-3}}}{\mathrm{mol\,dm^{-3}}}$$

$$K_a = \frac{\mathrm{mol\,dm^{-3}} \times \cancel{\mathrm{mol\,dm^{-3}}}}{\cancel{\mathrm{mol\,dm^{-3}}}}$$

$$K_a = \mathrm{mol\,dm^{-3}}$$

Large K_a	**Large dissociation - Strong acid**
Small K_a	**Small dissociation - Weak acid**

K_a and pK_a - a compressed scale:

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

- Just like the pH scale it is more useful to compress the scale.
- To keep it simple we use the same logarithmic scale when dealing with K_a values.
- Now, instead of pH we have **pK_a :**

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

- If it is a **strong acid** then it will dissociate a lot. This gives a large top number and a small bottom number.
- This will give a **large K_a** value, but a **small pK_a**
- If it is a **weak acid** then it will dissociate a little. This gives a small value on the top and a large bottom number.
- This will give a **small K_a** value, but a l**arge pK_a**

Calculating the pH for weak acids

- The pH of a weak acid is more difficult to calculate as the acid does not completely dissociate.

$HA_{(aq)}$	$\leftrightarrows$	$H^+_{(aq)}$	+	$A^-_{(aq)}$
1M		**0M**		**0M**
0.99M		**0.01M**		**0.01M**

- The **$[H^+_{(aq)}]$** is not the same as the **$[HA_{(aq)}]$**
- It is calculated in 2 steps:

Step 1: $[H^+_{(aq)}]$ must be calculated from the acid equilibrium expression, **K_a:**

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

- In order to calculate the **$[H^+_{(aq)}]$** we have to make a couple of assumptions: **LEARN**

1) For a weak acid: **$[H^+_{(aq)}] = [A^-_{(aq)}]$** - as both have been formed from the dissociation of the acid.

2) $[HA_{(aq)}]$ remains unchanged - a weak acid dissociates so little that the concentration remains virtually the same.

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

- Rearrange to get:

$$[H^+]^2 = K_a \times [HA]$$

$$[H^+] = (K_a \times [HA])^{0.5}$$

Step 2: $[H^+_{(aq)}]$ is put in the pH formula: **$pH = -\log_{10}[H^+_{(aq)}]$**

Example: Calculate the pH of a 0.100 mol dm^{-3} ethanoic acid, $K_a = 1.7 \times 10^{-5}$ mol dm^{-3}

- Write the equation for the dissociation of the acid:

$$CH_3COOH_{(l)} \leftrightarrows H^+_{(aq)} + CH_3COO^-_{(aq)}$$

Step 1: $[H^+_{(aq)}]$ must be calculated from the acid equilibrium expression, **K_a:**

$$K_a = \frac{[H^+] \times [CH_3COO^-]}{[CH_3COOH]}$$

- Apply the assumptions:

1) $[H^+_{(aq)}] = [CH_3COO^-]$

2) $[CH_3COOH]$ remains unchanged

$$K_a = \frac{[H^+]^2}{[CH_3COOH]}$$

- Put in the numbers:

$$1.7 \times 10^{-5} = \frac{[H^+]^2}{0.100}$$

- Rearrange:

$$[H^+]^2 = 1.7 \times 10^{-5} \times 0.100$$

- Take the square root:

$$[H^+] = 1.304 \times 10^{-3} \text{ mol dm}^{-3}$$

- Now put the $[H^+_{(aq)}]$ in the pH formula:

$$pH = -\log_{10}[H^+_{(aq)}]$$
$$pH = -\log_{10} [1.3 \times 10^{-3}]$$
$$pH = 2.88$$

Summary:

Step 1: Calculate $[H^+_{(aq)}]$

$$[H^+] = (K_a \times [HA])^{0.5}$$

Applying assumptions:

1) $[H^+_{(aq)}] = [A^-_{(aq)}]$

2) $[HA_{(aq)}]$ remains unchanged

Step 2: Calculate pH

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

Calculating K_a for weak acids

- This can of course work the other way to calculate the K_a of a weak acid
- For this we need:

1) pH of the weak acid

2) Concentration of the weak acid

- Again is is done in 2 steps:

Step 1: Calculate $[H^+_{(aq)}]$

- This is done from the pH and working backwards:

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

Step 2: Calculate K_a

- Put the **$[H^+]$** and **$[HA]$** to calculate **K_a**

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

Example - Calculate K_a for 0.03 mol dm^{-3} methanoic acid, pH = 2.66

Step 1: Calculate $[H^+_{(aq)}]$

$$[H^+] = 10^{-pH}$$
$$[H^+] = 10^{-2.66}$$
$$[H^+] = 2.19 \times 10^{-3}$$

Step 2: Calculate K_a

- Put the **$[H^+]$** and **$[HA]$** to calculate **K_a**

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

- Put values in:

$$K_a = \frac{[2.19 \times 10^{-3}]^2}{[0.03]}$$

$$K_a = 1.6 \times 10^{-4} \text{ Mol dm}^{-3}$$

Buffer solutions

A buffer solution minimises the change in pH with the small addition of acids or bases

- These are important in controlling the pH in living systems.
- Buffer solutions are made:

1) Weak acid, HA

2) Conjugate base of the weak acid, A^-

- Ethanoic acid is a weak acid being only slightly ionised in solution
- The equilibrium lies over to the left:

$$CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$$

- What would happen if more ethanoate ions were added to the solution.
- This can be done by adding a small amount of sodium ethanoate which is highly ionised in solution:

$$CH_3COO^- Na^+_{(aq)} \rightarrow Na^+_{(aq)} + CH_3COO^-_{(aq)}$$

Alternativily:

- Buffer solutions can also be made by partially neutralising an acid:

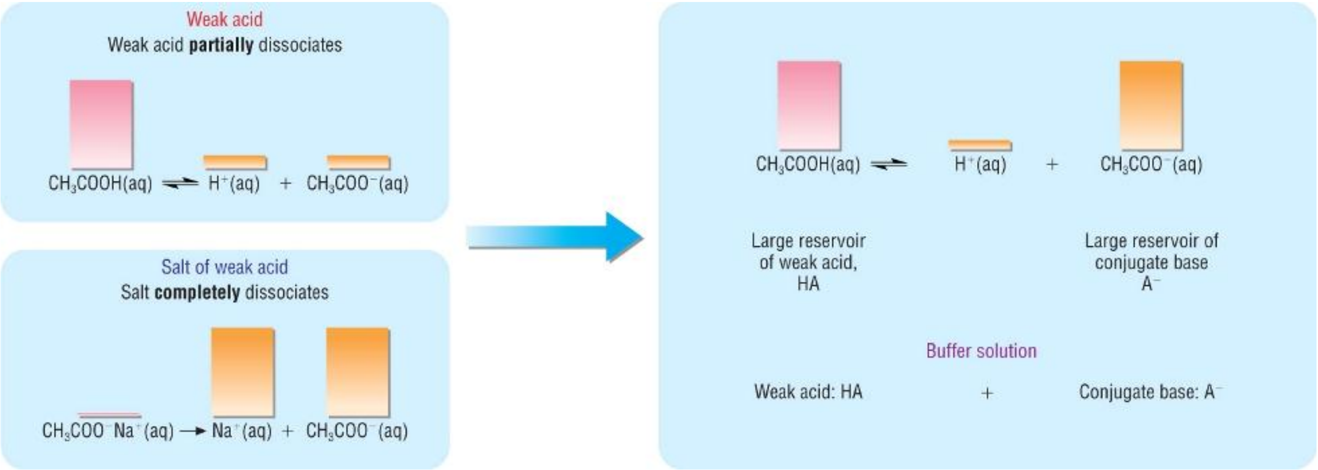
$$HCOOH_{(aq)} + NaOH_{(aq)} \rightarrow HCOO^- Na^+_{(aq)} \qquad + \qquad H_2O$$

- This leaves some of the acid to dissociate partially:

$$HCOOH_{(aq)} \rightleftharpoons H^+_{(aq)} + HCOO^-_{(aq)}$$

- It also produces the ionic salt which dissociates fully in solution:

$$HCOO^- Na^+_{(aq)} \rightarrow Na^+_{(aq)} + HCOO^-_{(aq)}$$



- This gives you an equilibrium with a large amount of acid **and the conjugate base**.
- The high concentration of the conjugate base pushes the **acid equilibrium over to the LHS**.
- This means that the **$[H^+_{(aq)}]$ will be very small**.

How does a buffer act?

- The 2 reactions needed to explain how they work are outlined below:

$HA_{(aq)} \leftrightarrows H^+_{(aq)} + A^-_{(aq)}$ **Reaction 1**

$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$ **Reaction 2**

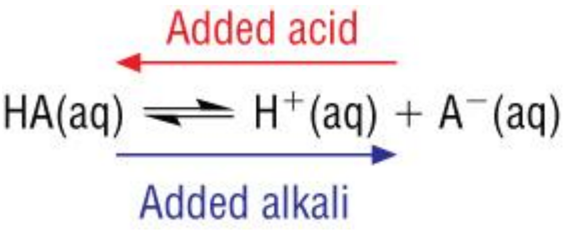
Addition of and acid, H^+ ions:

- Addition of **H^+ ions** increases the **$[H^+]$**
- This moves the equilibrium of **Reaction 1** to the **left hand side**
- This reduces the **$[H^+]$** thus restoring the pH.

Addition of an alkali, OH^- ions:

- **OH^- ions** reacts with **H^+ ions** in **Reaction 1 according to Reaction 2** forming water.
- This reduces the **$[H^+]$** in **Reaction 1**.
- The equilibrium in **Reaction 1** moves to the **right hand side** replacing the H^+ used, thus restoring the pH

Overall:



pH values of buffer solutions

Calculations involving buffer solutions

- We can calculate the pH of a buffer solution if we are given:

1) Ka of the weak acid

2) Equilibrium concentrations of the conjugate acid - base pair

Method 1:

1) Write the reaction:

$$HA_{(aq)} \leftrightarrows H^+_{(aq)} + A^-_{(aq)}$$

2) Write the equilibrium expression, K_a

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

- **Remember $[H^+]$ does not equal $[A^-]$ as $[A^-]$ is determined from the conjugate base**

3) Rearrange the equation to calculate the hydrogen concentration

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

- **2 assumptions are made here**

1) [HA] remains unchanged as it dissociates by such a small amount

2) $[A^-] = [NaA]$ as is dissociates fully

4) calculate the pH

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

Example:

- A buffer solution contains 0.600 Mol dm^{-3} propanoic acid and 0.800 Mol dm^{-3} sodium propanoate.
- The equilibrium constant, K_a for propanoic acid = 1.3 x 10^{-5} Mol dm^{-3}.
- Calculate the pH of the buffer solution:

1) Write the reaction:

$$C_2H_5COOH_{(aq)} \leftrightarrows H^+_{(aq)} + C_2H_5COO^-_{(aq)}$$

2) Write the equilibrium expression, K_a

$$K_a = \frac{[H^+] \times [C_2H_5COO^-]}{[C_2H_5COOH]}$$

3) Rearrange the equation to get the hydrogen ion concentration:

$$[H^+] = K_a \times \frac{[C_2H_5COOH]}{[C_2H_5COO^-]}$$

$$[H^+] = 1.3 \times 10^{-5} \times \frac{0.600}{0.800}$$

$$[H^+] = 9.75 \times 10^{-6}$$

6) calculate the pH

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

$$pH = -\log_{10}[9.75 \times 10^{-6}]$$

$$pH = 5.01$$

Alternative Method 2: Recommended for non mathematicians

- Use theHenderson - Hasselbalch relationship:

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

$$pH = -\log K_a + \log \frac{[C_2H_5COO^-]}{[C_2H_5COOH]}$$

$$pH = -\log 1.3 \times 10^{-5} + \log \frac{[0.800]}{[0.600]}$$

$$pH = 5.01$$

The carbonic acid - hydrogen carbonate buffer system

- The pH of blood needs to be between 7.35 - 7.45.
- This is controlled by a mixture of buffers but the carbonic acid buffer is the most important:

Carbonic acid: H_2CO_3 and its conjugate base: HCO_3^-

- The 2 reactions needed to explain how this buffer works is outlined below:

$H_2CO_{3(aq)} \leftrightarrows H^+_{(aq)} + HCO_3{}^-_{(aq)}$ **Reaction 1**

$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$ **Reaction 2**

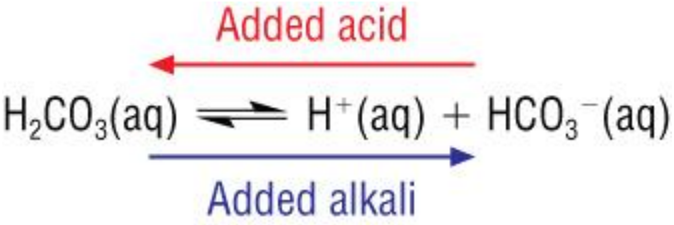
Addition of and acid, H^+ ions:

- Addition of **H^+ ions** increases the **$[H^+]$**
- This moves the equilibrium of **Reaction 1** to the **left hand side**
- This reduces the **$[H^+]$** thus restoring the pH.

Addition of an alkali, OH^- ions:

- **OH^- ions** reacts with **H^+ ions** in **Reaction 1 according to Reaction 2** forming water.
- This reduces the **$[H^+]$** in **Reaction 1**.
- The equilibrium in **Reaction 1** moves to the **right hand side** replacing the H^+ used, thus restoring the pH

Overall:



- Most materials released into the blood is acidic.
- This is removed by the conversion into carbonic acid.
- **Enzymes** convert the carbonic acid into dissolved **CO_2** which is released as a gas through the lungs:

$CO_{2(aq)} \leftrightarrows CO_{2(g)}$

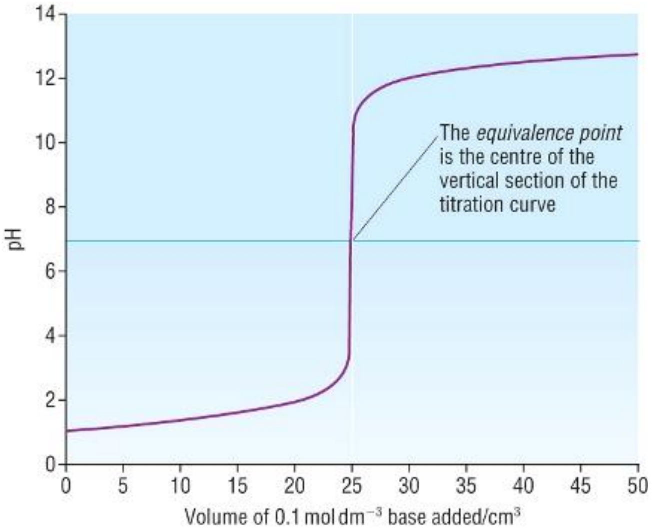
- The amount of **CO_2** is controlled by breathing. Breathing heavily removes more **CO_2** from the blood.

Neutralisation - titration curves

Titrations for AS chemistry

- During titrations you are measuring the exact volume of one solution that reacts with a known volume of another.
- This is called the **equivalence point**.
- **Acid - base titrations** deals with the **pH changes** that occur during the movement from **acid** → **base** and from **base** → **acid**

Key features of titration curves - for a base added to an acid:



- When the base is first added, the **pH increases very slightly** due to the large excess of acid, the gradually increases.
- **Within a drop**, the **pH increases** sharply from **below 7 to above 7, the middle of this section is the equivalence point.**
- With continual addition of base, the increase in **pH** tails of until the **increases is again very slight.**

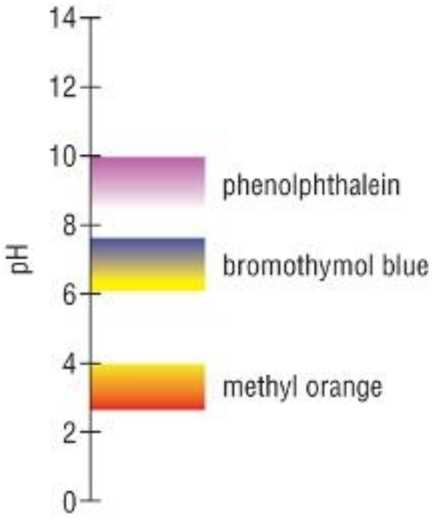
Choosing the indicator

- Many dyes are affected by pH as they are themselves weak acids.
- This means that they will themselves be subject to shifts in their equilibrium with the addition of H^+ or OH^-.
- This will then correspond to a colour change.
- They are often considered to be weak acids where the acid or corresponding base are both coloured.
- Consider an indicator, HIn

$$\mathbf{HIn_{(aq)}} \rightleftarrows \mathbf{H^+_{(aq)}} + \mathbf{In^-_{(aq)}}$$

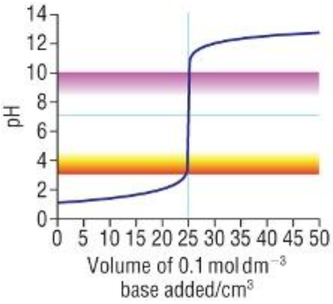
- Addition of an acid will move the equilibrium to the reactants. This shifts to the **RED**
- Addition of a base removes $H^+_{(aq)}$ which moves the equilibrium to the products. This shifts to the **YELLOW**
- When the **[HIn] = [In$^-$]** the indicator is at its **end point**
- Most indicators change colour over a couple of pH units.
- **The end point** for chemical indicators is **in the middle** of the pH range.

Indicator and titration curves



- The **equivalence point** of any neutralisation reaction is **pH7**
- The **end point** (colour change) in indicators do not necessarily correspond to the **equivalence point**
- Look at **methyl orange** - it changes colour in the **pH** range of **2.8 - 4.0**.
- This means that the **end point** does not necessarily correspond to the **equivalence point for some neutralisation reactions**

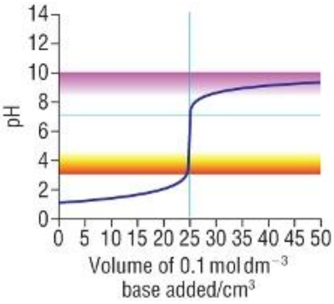
- **Acids and alkalis can be strong or weak which gives us 4 types of neutralisation:**



Strong acid – Strong base

Phenylphthalein - Suitable

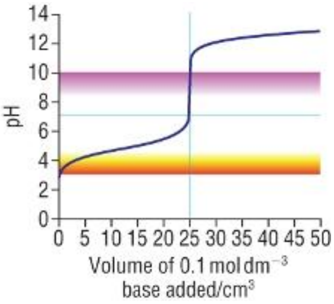
Methyl orange - Suitable



Strong acid – Weak base

Phenylphthalein - Unsuitable

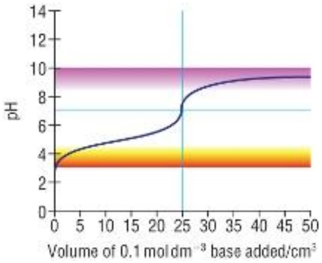
Methyl orange - Suitable



Weak acid – Strong base

Phenylphthalein - Suitable

Methyl orange - Unsuitable



Weak acid – Weak base

Phenylphthalein - Unsuitable

Methyl orange - Unsuitable

- **Weak acids - weak alkalis are not titrated against each other due to the short pH change during neutralisation**

Neutralisation - enthalpy changes

Standard enthalpy change of neutralisation

- Consider the neutralisation of aqueous acid with aqueous base:

Full: $HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$

Ions: $H^+_{(aq)} + Cl^-_{(aq)} + Na^+_{(aq)} + OH^-_{(aq)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)} + H_2O_{(l)}$

Ionic: $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$

- $Na^+_{(aq)}$ and $Cl^-_{(aq)}$ are **spectator ions** and do not take part in the reaction.
- The enthalpy change for this is the **enthalpy change of neutralisation:**

Is the energy change when aq acid is neutralised by aq base forming 1 mole of water under standard conditions

Determination of enthalpy change of neutralisation:

Example:

25cm^3 of 2M nitric acid is added to 25cm^3 of 2M potassium hydroxide. The temperature increases from 22.0 ^{o}C to 35.5 ^{o}C.
Calculate the enthalpy change of neutralisation:

1) The energy change:

Q =	**m**	**x c x ΔT**
Q =	**50**	**x 4.18 x 13.5**
Q =	**50**	**x 4.18 x 13.5**
Q =	**2821.5 Joules**	**Exothermic so will be negative:**
Q =	**- 2821.5 Joules**	

2) Calculate the number of moles used:

$$\text{Moles } (HNO_3) = \frac{C \times V}{1000} \qquad \text{Moles } (KOH) = \frac{C \times V}{1000}$$

$$\text{Moles } (HNO_3) = \frac{2 \times 25}{1000} \qquad \text{Moles } (KOH) = \frac{2 \times 25}{1000}$$

$$\text{Moles } (HNO_3) \quad 0.0500 \qquad \text{Moles } (KOH) \quad 0.0500$$

3) Calculate the amount of energy exchanged per mole of water, enthalpy change of neutralisation:

$$\text{Enthalpy} = \frac{\text{Energy}}{\text{Moles}}$$

$$\text{Enthalpy} = \frac{-\ 2821.5}{0.0500}$$

Enthalpy = - 56430 j Mol^{-1}

Enthalpy = - 56.4 Kj Mol^{-1}

- The number of moles of **acid : alkalil : water** are the same for monobasic acids

Comparisons of enthalpy changes of neutralisation of different acids:

Acid	Reaction	ΔH^{θ}_{neut} / Kj Mol^{-1}
Hydrochloric acid	**Full:** $HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$ **Ionic:** $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$	**- 57.9**
Nitric acid	**Full:** $HNO_{3(aq)} + NaOH_{(aq)} \rightarrow NaNO_{3(aq)} + H_2O_{(l)}$ **Ionic:** $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$	**- 57.6**
Hydrobromic acid	**Full:** $HBr_{(aq)} + NaOH_{(aq)} \rightarrow NaBr_{(aq)} + H_2O_{(l)}$ **Ionic:** $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$	**- 57.6**
Ethanoic acid	**Full:** $CH_3COOH_{(aq)} + NaOH_{(aq)} \rightarrow CH_3COONa_{(aq)} + H_2O_{(l)}$ **Ionic:** $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$	**- 57.1**

- Note that they are all around the same enthalpy changes.
- This is due to the fact that it is essentially the same ionic reaction once the spectator ions have been removed
- Ethanoic acid has a slightly lower enthalpy change due to the fact that ethanoic acid has to dissociate as the reaction proceeds.
- This means that the reaction is slower so energy is lost as it proceeds at a slower rate.