5.1.3 Acids, Bases and Buffers

Bronsted-Lowry Definition of Acid - Base behaviour

A **Bronsted-Lowry acid** is defined as a substance that can **donate a proton**.
A **Bronsted-Lowry base** is defined as a substance that can **accept a proton**.

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

Acid 1 base 2 Acid 2 Base 1

Each acid is linked to a conjugate base on the other side of the equation.

$HNO_3 + HNO_2 \rightleftharpoons NO_3^- + H_2NO_2^+$

Acid 1 Base 2 Base 1 Acid 2

$HCOOH + CH_3(CH_2)_2COOH \rightleftharpoons HCOO^- + CH_3(CH_2)_2COOH_2^+$

Acid 1 Base 2 Base 1 Acid 2

In these reactions the substance with bigger K_a will act as the acid

The acidic role of H$^+$ in the reactions of acids with metals, carbonates, bases and alkalis

Ionic Equations

acid + metal → salt + hydrogen

$2CH_3CH_2CO_2H + Mg \rightarrow (CH_3CH_2COO)_2Mg + H_2$ ⟶ $2H^+ + Mg \rightarrow Mg^{2+} + H_2$

acid + alkali (NaOH) → salt + water

$2HNO_2 + Ca(OH)_2 \rightarrow Ca(NO_2)_2 + 2H_2O$ ⟶ $H^+ + OH^- \rightarrow H_2O$

acid + carbonate (Na_2CO_3) → salt + water + CO_2

$2CH_3CO_2H + Na_2CO_3 \rightarrow 2CH_3CO_2^-Na^+ + H_2O + CO_2$ ⟶ $2H^+ + CO_3^{2-} \rightarrow H_2O + CO_2$

Calculating pH

pH = - log [H$^+$]

Where [H$^+$] is the concentration of hydrogen ions in the solution

Calculating pH of strong acids

Strong acids **completely dissociate**

The concentration of hydrogen ions in a monoprotic strong acid will be the same as the concentration of the acid.

For HCl and HNO_3 the [H$^+$(aq)] will be the same as the original concentration of the acid.

For 0.1M HCl the pH will be –log[0.1] =1.00

Always give pH values to **2d.p**. In the exam

Finding [H$^+$] from pH

[H$^+$] = 1 x 10^{-pH}

On most calculators this is done by pressing

Inv (or 2nd function)→ log → - number(pH)

Example 1

Calculate the concentration of HCl with a pH of 1.35

[H$^+$] = 1 x 10$^{-1.35}$ = 0.045M

Ionic product for water

In all aqueous solutions and pure water the following equilibrium occurs: $H_2O\ (l) \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$

This equilibrium has the following equilibrium expression

$$K_c = \frac{[H^+_{(aq)}][OH^-_{(aq)}]}{[H_2O(l)]} \longrightarrow K_c \times [H_2O\ (l)] = [H^+_{(aq)}][OH^-_{(aq)}] \longrightarrow \boxed{\mathbf{K_w = [H^+_{(aq)}][OH^-_{(aq)}]}}$$

Rearrange to

Because $[H_2O\ (l)]$ is much bigger than the concentrations of the ions, we assume its value is constant and make a new constant Kw

Learn this expression

At 25°C the value of K_w for all aqueous solutions is 1×10^{-14} mol^2dm^{-6}

The K_w expression can be used to calculate $[H^{+\ (aq)}]$ ions if we know the $[OH^{-\ (aq)}]$ ions and vice versa

Finding pH of pure water

Pure water/ neutral solutions are **neutral** because the $\mathbf{[H^+_{(aq)}] = [OH^-_{(aq)}]}$
Using $K_w = [H^+_{(aq)}][OH^-_{(aq)}]$ then when neutral $K_w = [H^+_{(aq)}]^2$
and $[H^+_{(aq)}] = \sqrt{K_w}$
At 25°C $[H^+_{(aq)}] = \sqrt{1\times10^{-14}} = 1\times10^{-7}$ so pH = 7

Example 2 : Calculate the pH of water at 50°C given that $K_w = 5.476 \times 10^{-14}$ $mol^2\ dm^{-6}$ at 50°C
$[H^+_{(aq)}] = \sqrt{K_w} = \sqrt{5.476 \times 10^{-14}} = 2.34 \times 10^{-7}$ mol dm^{-3}
pH = - log 2.34×10^{-7} = 6.6
It is still neutral though as $[H^+_{(aq)}] = [OH^-_{(aq)}]$

At different temperatures to 25°C the pH of pure water changes. Le Chatelier's principle can predict the change. The dissociation of water is endothermic (because bonds are broken) so increasing the temperature would push the equilibrium to the right giving a bigger concentration of H^+ ions and a lower pH

Calculating pH of strong base

For bases we are normally given the concentration of the hydroxide ion.

To work out the pH we need to work out $[H^+(aq)]$ using the K_w expression.

Strong bases completely dissociate into their ions.
$NaOH \rightarrow Na^+ + OH^-$

Example 3:

Calculate the pH of the strong base 0.1 mol dm^{-3} NaOH

Assume complete dissociation.

$K_w = [H^{+\ (aq)}][OH^{-\ (aq)}] = 1\times10^{-14}$

$[H^+(aq)] = K_w / [OH^{-\ (aq)}] = 1\times10^{-14} / 0.1 = 1\times10^{-13}$ mol dm^{-3}

pH = - log$[1\times10^{-13}]$ =**13.00**

Weak acids

Weak acids only **slightly dissociate** when dissolved in water, giving an equilibrium mixture

$HA + H_2O(l) \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$ We can simplify this to $\longrightarrow$ $HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$

Weak acids dissociation expression

$$K_a = \frac{[H^+_{(aq)}][A^-_{(aq)}]}{[HA\ (aq)]}$$

The K_a for ethanoic acid is 1.7×10^{-5} mol dm^{-3}.

The larger K_a the stronger the acid.

Example 4 Write an equation for dissociation of propanoic acid and its K_a expression

$CH_3CH_2CO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3CH_2CO_2^-{}_{(aq)}$

$$K_a = \frac{[H^+_{(aq)}][CH_3CH_2CO_2^-{}_{(aq)}]}{[CH_3CH_2CO_2H_{(aq)}]}$$

pK_a

Sometimes K_a values are quoted as pK_a values

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

Calculating pH of a weak acid

To make the calculation easier two assumptions are made to simplify the K_a expression:

1) $[H^+_{(aq)}]_{eqm} = [A^-_{(aq)}]_{eqm}$ because they have dissociated according to a 1:1 ratio

2) As the amount of dissociation is small we assume that the initial concentration of the undissociated acid has remained constant.

So $[HA_{(aq)}]_{eqm} = [HA_{(aq)}]_{initial}$

$$K_a = \frac{[H^+_{(aq)}][A^-_{(aq)}]}{[HA\ (aq)]}$$

Simplifies to $\downarrow$

$$K_a = \frac{[H^+_{(aq)}]^2}{[HA_{(aq)}]_{initial}}$$

Example 5 Calculate the pH of a solution of 0.01 mol dm^{-3} ethanoic acid (K_a is 1.7×10^{-5} mol dm^{-3})

$CH_3CO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3CO_2^-{}_{(aq)}$

$$K_a = \frac{[H^+_{(aq)}][CH_3CO_2^-{}_{(aq)}]}{[CH_3CO_2H_{(aq)}]} \longrightarrow K_a = \frac{[H^+_{(aq)}]^2}{[CH_3CO_2H_{(aq)}]_{initial}} \rightarrow 1.7 \times 10^{-5} = \frac{[H^+_{(aq)}]^2}{0.01}$$

$[H^+_{(aq)}]^2 = 1.7 \times 10^{-5} \times 0.01$

$[H^+_{(aq)}] = \sqrt{1.7 \times 10^{-7}} = 4.12 \times 10^{-4}$

pH = - log [H$^+$] = -log (4.12×10^{-4})

pH =3.38

Example 6 Calculate the concentration of propanoic acid with a pH of 3.52 (K_a is 1.35×10^{-5} mol dm^{-3})

$CH_3CH_2CO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3CH_2CO_2^-{}_{(aq)}$

$[H^+] = 1 \times 10^{-3.52} = 0.000302$M

$$K_a = \frac{[H^+_{(aq)}][CH_3CH_2CO_2^-{}_{(aq)}]}{[CH_3CH_2CO_2H_{(aq)}]} \longrightarrow K_a = \frac{[H^+_{(aq)}]^2}{[CH_3CH_2CO_2H_{(aq)}]_{initial}} \rightarrow 1.35 \times 10^{-5} = \frac{[0.000302]^2}{[CH_3CH_2CO_2H_{(aq)}]_{initial}}$$

$[CH_3CH_2CO_2H_{(aq)}] = 9.12 \times 10^{-8} / 1.35 \times 10^{-5}$

$[CH_3CH_2CO_2H_{(aq)}] = 6.75 \times 10^{-3}$ mol dm^{-3}

Diluting an acid or alkali

pH of diluted strong acid

$$[H^+] = [H^+]_{old} \times \frac{\text{old volume}}{\text{new volume}}$$

$$pH = -\log [H^+]$$

pH of diluted base

$$[OH^-] = [OH^-]_{old} \times \frac{\text{old volume}}{\text{new volume}}$$

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

$$pH = -\log [H^+]$$

Example 7 Calculate the new pH when 50.0 cm^3 of 0.150 mol dm^{-3} HCl is mixed with 500 cm^3 of water.

$$H^+] = [H^+]_{old} \times \frac{\text{old volume}}{\text{new volume}}$$

$$[H^+_{(aq)}] = 0.150 \times \frac{0.05}{0.55}$$

$[H^+_{(aq)}] = 0.0136$

pH = $-\log [H^+]$

= -log 0.0136

= 1.87

Buffer Solutions

A buffer solution is one where the pH does **not change significantly** if **small** amounts of acid or alkali are added to it.

An **acidic** buffer solution is made from a **weak acid** and a **salt of that weak acid** (made from reacting the weak acid with a strong base)

Example : ethanoic acid and sodium ethanoate

$CH_3CO_2H_{(aq)}$ and $CH_3CO_2^- Na^+$

A **basic** buffer solution is made from a weak base and a salt of that weak base (made from reacting the weak base with a strong acid)

Example :ammonia and ammonium chloride

NH_3 and $NH_4^+Cl^-$

The salt content can be added in several ways: a salt solution could be added to the acid or some solid salt added. A buffer can also be made by partially neutralising a weak acid with alkali and therefore producing a mixture of salt and acid

How buffer solutions work

In an ethanoic acid buffer

$$CH_3CO_2H_{(aq)} \rightleftharpoons CH_3CO_2^-{}_{(aq)} + H^+_{(aq)}$$

Acid conjugate base

In a buffer solution there is a much higher concentration of the salt $CH_3CO_2^-$ ion than in the pure acid.

If **small amounts of acid is added** to the buffer: Then the above equilibrium will shift to the left removing nearly all the H^+ ions added, $CH_3CO_2^-{}_{(aq)} + H^+_{(aq)} \rightarrow CH_3CO_2H_{(aq)}$

As there is a large concentration of the salt ion in the buffer the ratio $[CH_3CO_2H]/ [CH_3CO_2^-]$ stays almost constant, so the pH stays fairly constant.

If **small amounts of alkali is added** to the buffer. The OH^- ions will react with H^+ ions to form water. The Equilibrium will then shift to the right to produce more H^+ ions. Overall the concentration of H^+ ions and pH remains constant (but some ethanoic acid molecules are changed to ethanoate ions)

$$CH_3CO_2H_{(aq)} \rightleftharpoons CH_3CO_2^-{}_{(aq)} + H^+_{(aq)}$$

Learn these explanations carefully and be able to write the equilibrium to illustrate your answer

Calculating the pH of buffer solutions

We still use the weak acids dissociation expression

$$K_a = \frac{[H^+_{(aq)}][A^-_{(aq)}]}{[HA_{(aq)}]}$$

But here we assume the $[A^-]$ concentration is due to the added salt only

Normally we rearrange to →

$$[H^+_{(aq)}] = K_a \frac{[HA_{(aq)}]}{[A^-_{(aq)}]}$$

We also assume the Initial concentration of the acid has remained constant, because amount that has dissociated or reacted is small

Example 8: making a buffer by adding a salt solution

Calculate the pH of a buffer made from 45 cm^3 of 0.10 mol dm^{-3} ethanoic acid and 50cm^3 of 0.15 mol dm^{-3} sodium ethanoate ($K_a = 1.7 \times 10^{-5}$)

Calculate the moles of both solutions
Moles ethanoic = conc x vol = 0.1 x 0.045 = 0.0045 mol
Moles sodium ethanoate = conc x vol = 0.15 x 0.050 = 0.0075 mol

$$[H^+_{(aq)}] = K_a \frac{[HA_{(aq)}]}{[A^-_{(aq)}]}$$

We can enter moles of acid and salt straight into the equation as they both have the same new final volume

$$[H^+_{(aq)}] = 1.7 \times 10^{-5} \times \frac{0.0045}{0.0075} \rightarrow [H^+_{(aq)}] = 1.02 \times 10^{-5}$$

$pH = -\log [H^+]$
$= -\log 1.02 \times 10^{-5}$
$= 4.99$

Example 9 : making a buffer by adding a solid salt

A buffer solution is made by adding 1.1 g of sodium ethanoate into 100 cm^3 of 0.4 mol dm^{-3} ethanoic acid. Calculate its pH. $K_a = 1.7 \times 10^{-5}$ mol dm^{-3}

Work out the moles of both solutions
Moles ethanoic = conc x vol = 0.4 x 0.1 = 0.04 mol
Moles sodium ethanoate = mass/M_r= 1.1/82 = 0.0134 mol

$$[H^+_{(aq)}] = K_a \frac{[HA_{(aq)}]}{[A^-_{(aq)}]}$$

We can enter moles of acid and salt straight into the equation as they both have the same new final volume

$$[H^+_{(aq)}] = 1.7 \times 10^{-5} \times \frac{0.04}{0.0134} \rightarrow [H^+_{(aq)}] = 5.07 \times 10^{-5}$$

$pH = -\log [H^+]$
$= -\log 5.07 \times 10^{-5}$
$= 4.29$

If a buffer is made by adding sodium hydroxide to partially neutralise a weak acid then follow the method below

Example 10 55cm^3 of 0.50 mol dm^{-3} CH_3CO_2H is reacted with 25cm^3 of 0.35 mol dm^{-3} NaOH. Calculate the pH of the resulting buffer solution.

$CH_3CO_2H + NaOH \rightarrow CH_3CO_2Na + H_2O$

K_a is 1.7×10^{-5} mol dm^{-3}

Moles CH_3CO_2H = conc x vol =0.50x 0.055 = 0.0275mol
Moles NaOH = conc x vol = 0.35 x 0.025 = 0.00875 mol

Moles of CH_3CO_2H in excess = 0.0275-0.00875 = 0.01875 (as 1:1 ratio)

$$[CH_3CO_2H] = \frac{\text{moles excess } CH_3CO_2H}{\text{total volume } (dm^3)}$$

$= 0.01875/\ 0.08 = 0.234$ mol dm^{-3}

$$[CH_3CO_2^-] = \frac{\text{moles } OH^- \text{ added}}{\text{total volume } (dm^3)}$$

$= 0.00875/\ 0.08 = 0.109$ mol dm^{-3}

$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]}$$

$[H^+] = K_a \times [CH_3CO_2H] / [CH_3CO_2^-]$
$= 1.7 \times 10^{-5} \times 0.234 / 0.109$
$= 3.64 \times 10^{-5}$

$pH = -\log [H^+]$
$= -\log 3.64 \times 10^{-5}$
$= 4.44$

Calculating change in pH of buffer on addition of small amount of acid or alkali

If a small amount of alkali is added to a buffer then the moles of the buffer acid would reduce by the number of moles of alkali added and the moles of salt would increase by the same amount so a new calculation of pH can be done with the new values

$$CH_3CO_2H_{(aq)} + OH^- \rightarrow CH_3CO_2^-{}_{(aq)} + H_2O_{(l)}$$

If a small amount of acid is added to a buffer then the moles of the buffer salt would reduce by the number of moles of acid added and the moles of buffer acid would increase by the same amount so a new calculation of pH can be done with the new values.

$$CH_3CO_2^-{}_{(aq)} + H^+ \rightarrow CH_3CO_2H_{(aq)}$$

Example 11: 0.005 mol of NaOH is added to 500cm^3 of a buffer where the concentration of ethanoic acid is 0.200 mol dm^{-3} and the concentration of sodium ethanoate is 0.250 mol dm^{-3} ($K_a = 1.7 \times 10^{-5}$ mol dm^{-3})
Calculate the pH of the buffer solution after the NaOH has been added.

Work out the moles of acid and salt in the initial buffer solution
Moles ethanoic acid= conc x vol = 0.200 x 0.500 = 0.100 mol
Moles sodium ethanoate = conc x vol = 0.25 x 0.500 = 0.125 mol

Work out the moles of acid and salt in buffer after the addition of 0.005mol NaOH
Moles ethanoic acid = 0.100 - 0.005 = 0.095 mol
Moles sodium ethanoate = 0.125 +0.005 = 0.130 mol

$$[H^+_{(aq)}] = K_a \frac{[CH_3COOH_{(aq)}]}{[CH_3COO^-{}_{(aq)}]}$$

We can enter moles of acid and salt straight into the equation as they both have the same new final volume

$$[H^+_{(aq)}] = 1.7 \times 10^{-5} \times \frac{0.095}{0.130} \rightarrow [H^+_{(aq)}] = 1.24 \times 10^{-5}$$

$$\text{pH} = -\log [H^+] = -\log 1.24 \times 10^{-5} = 4.91$$

Buffering action in blood

A carbonic acid– hydrogencarbonate equilibrium acts as a buffer in the control of blood pH

The H_2CO_3/HCO_3^- buffer is present in blood plasma, maintaining a pH between 7.35 and 7.45.

Equilibrium
$H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq)$

Adding alkali reacts with H$^+$ with the equation
$H^+ + OH^- \rightarrow H_2O$
so the above equilibrium would shift right forming new H$^+$ and more HCO_3^-

Adding acid shifts the above equilibrium left.
The reaction is
$H^+ + HCO_3^- \rightarrow H_2CO_3$

Titration curves

Constructing a pH curve

1. Transfer 25cm^3 of acid to a conical flask with a volumetric pipette
2. Measure initial pH of the acid with a pH meter
3. Add alkali in small amounts (2cm^3) noting the volume added
4. Stir mixture to equalise the pH
5. Measure and record the pH to 1 d.p.
6. Repeat steps 3-5 but when approaching endpoint add in smaller volumes of alkali
7. Add until alkali in excess

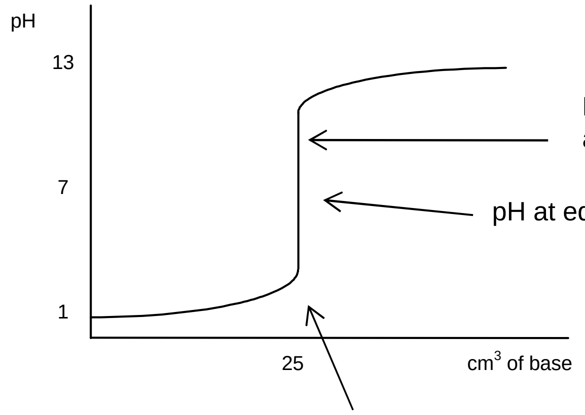
Calibrate meter first by measuring known pH of a buffer solution. This is necessary because pH meters can lose accuracy on storage.
Most pH probes are calibrated by putting probe in a set buffer (often pH 4) and pressing a calibration button/setting for that pH. Sometimes this is repeated with a second buffer at a different pH

Can also improve accuracy by **maintaining** constant temperature

Strong acid – Strong base

e.g. HCl and NaOH

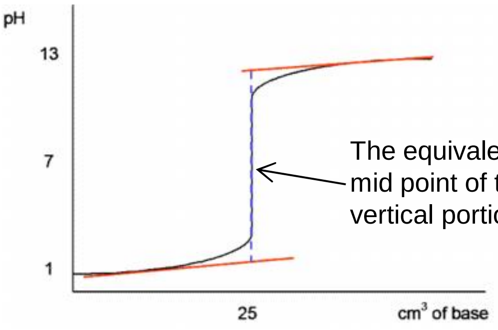
There are 4 main types of curve
1. Strong acid and strong base
2. Weak acid and strong base
3. Strong acid and weak base
4. Weak acid and weak base



Long steep part from around 3 to 9

pH at equivalence point = 7

You may also have to work out the neutralisation volume from titration data given in the question. These are done by standard titration calculations.



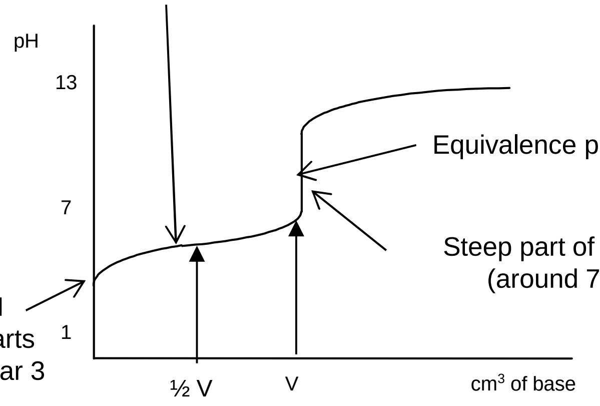
The equivalence point lies at the mid point of the extrapolated vertical portion of the curve.

The key points to sketching a curve:
Initial and final pH
Volume at neutralisation
General shape (pH at neutralisation)

Weak acid – Strong base

e.g. CH_3CO_2H and NaOH

At the start the pH rises quickly and then levels off. The flattened part is called the buffer region and is formed because a buffer solution is made



Equivalence point >7

Steep part of curve >7
(around 7 to 9)

pH
starts
near 3

Half neutralisation volume

For weak acids

$$K_a = \frac{[H^+{}_{(aq)}][A^-{}_{(aq)}]}{[HA\ (aq)]}$$

At ½ the neutralisation volume the [HA] = [A$^-$]

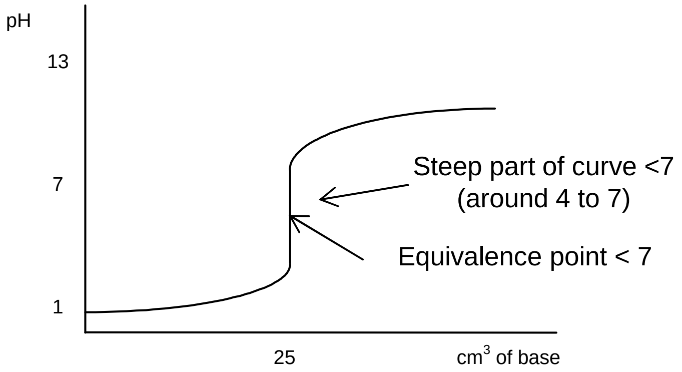
So K_a = [H$^+$] and pK_a = pH

If we know the K_a we can then work out the pH at ½ V or vice versa.

If a pH curve is plotted then the pH of a weak acid at half neutralisation (½ V) will equal the pK_a

Strong acid – Weak base

e.g. HCl and NH_3

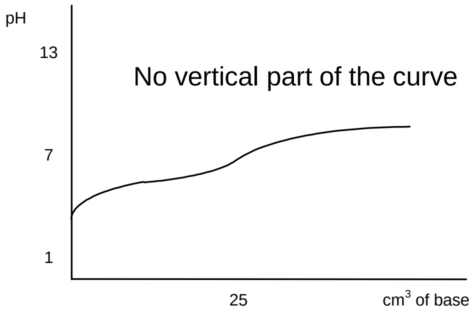


Steep part of curve <7 (around 4 to 7)

Equivalence point < 7

Weak acid – Weak base

e.g. CH_3CO_2H and NH_3



No vertical part of the curve

Choosing an Indicator

Indicators can be considered as weak acids. The acid must have a different colour to its conjugate base

An indicator changes colour from HIn to In^- over a narrow range. Different indicators change colours over different ranges.

The end-point of a titration is defined as the point when the colour of the indicator changes colour

The end-point of a titration is reached when [HIn] = [In^-]. To choose a correct indicator for a titration one should pick an indicator whose end-point coincides with the equivalence point for the titration.

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

colour A — colour B

We can apply Le Chatelier to give us the colour.

In an acid solution the H^+ ions present will push this equilibrium towards the reactants. Therefore colour A is the acidic colour.

In an alkaline solution the OH^- ions will react and remove H^+ ions causing the equilibrium to shift to the products. Colour B is the alkaline colour.

An indicator will work if the pH range of the indicator lies on the steep part of the titration curve. In this case the indicator will change colour rapidly and the colour change will correspond to the neutralisation point.

Only use phenolphthalein in titrations with strong bases but not weak bases.

Colour change: colourless acid → pink alkali

Use methyl orange with titrations with strong acids but not weak acids
Colour change: red acid → yellow alkali
(orange end point)