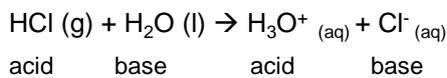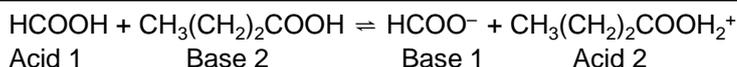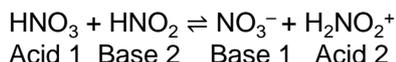# 14. Acid Base Equilibria

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   base   acid   base

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 Ka will act as the acid

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

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

On most calculators this is done by pressing

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

Example 1
What is the concentration of HCl with a pH of 1.35?
$[H^+] = 1 \times 10^{-1.35} = 0.045M$

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

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

$$Kc = \frac{[H^+_{(aq)}][OH^-_{(aq)}]}{[H_2O(l)]} \rightarrow Kc \times [H_2O\ (l)] = [H^+_{(aq)}][OH^-_{(aq)}] \rightarrow$$

$$Kw = [H^+_{(aq)}][OH^-_{(aq)}]$$

Learn this expression

At 25°C the value of Kw for all aqueous solutions is 1×10^{-14} mol²dm⁻⁶

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

pKw
Sometimes Kw is quoted as pKw values
$pKw = -\log Kw$ so $Kw = 10^{-pKw}$
If $Kw = 1 \times 10^{-14}$ then $pKw = 14$

Finding pH of pure water

Pure water/ neutral solutions are **neutral** because the $[H^+_{(aq)}] = [OH^-_{(aq)}]$
Using $Kw = [H^+_{(aq)}][OH^-_{(aq)}]$ then when neutral $Kw = [H^+_{(aq)}]^2$
and $[H^+_{(aq)}] = \sqrt{Kw}$
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
$[H^+_{(aq)}] = \sqrt{Kw} = \sqrt{5.476 \times 10^{-14}} = 2.34 \times 10^{-7}$ 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 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 kw expression.

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

Example 3: What is the pH of the strong base 0.1M NaOH

Assume complete dissociation.

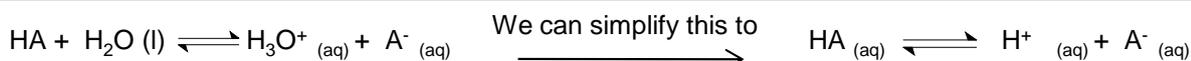$Kw = [H^{+\,(aq)}][OH^{-\,(aq)}] = 1\times10^{-14}$

$[H^+(aq)] = kw/ [OH^{-\,(aq)}] = 1\times10^{-14} / 0.1 = 1\times10^{-13}$ M

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 $HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$
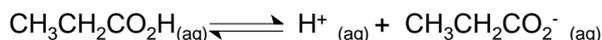
Weak acids dissociation expression

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

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

The larger ka the stronger the acid

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

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

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

pKa
Sometimes Ka values are quoted as pKa values
pKa = -log Ka   so Ka = 10^{-pKa}

Calculating pH of a weak acid

To make the calculation easier two assumptions are made to simplify the Ka 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.
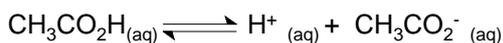
So $[HA_{(aq)}]_{eqm} = [HA_{(aq)}]_{initial}$

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

Simplifies to ↓

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

Example 5 What is the pH of a solution of 0.01M ethanoic acid (ka is 1.7×10^{-5} mol dm^{-3})?

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

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

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

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

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

pH = 3.38

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

$$CH_3CH_2CO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3CH_2CO_2^-_{(aq)}$$
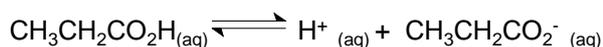
$$[H^+] = 1 \times 10^{-3.52} = 0.000302M$$

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

$$[CH_3CH_2CO_2H_{(aq)}] = 9.12 \times 10^{-8} / 1.35 \times 10^{-5} \qquad [CH_3CH_2CO_2H_{(aq)}] = 6.75 \times 10^{-3} M$$

Working out pH of a weak acid at half equivalence

When a weak acid has been reacted **with exactly half the neutralisation volume of alkali**, the above calculation can be simplified considerably.

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

At half neutralisation we can make the assumption that [HA] = [A-]

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

And **pH = pka**

Example 7

What is the pH of the resulting solution when **25cm^3 of 0.1M** NaOH is added to **50cm^3 of 0.1M** CH$_3$COOH (ka 1.7×10^{-5})

From the volumes and concentrations spot it is half neutralisation (or calculate)

pH = pka = -log (1.7×10^{-5}) = 4.77

Diluting an acid or alkali

pH of diluted strong acid

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

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

pH of diluted base

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

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

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

Example 8 Calculate the new pH when 50.0 cm^3 of 0.150 mol dm^{-3} HCl is mixed with 500 cm^3 of water.

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

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

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

pH = $-$ log [H$^+$]
= -log 0.0136
= 1.87

Comparing the pH of a strong acid and a weak acid after dilution 10, 100 and 1000 times

Because pH is a logarithmic scale, diluting a strong acid 10 times will increase its pH by one unit, and diluting it 100 times would increase its pH by two units

Weak acids would not change in the same way as when they are diluted. They increase by less than 1 unit
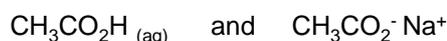
$$CH_3CH_2CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CH_2CO_2^-$$

Diluting the weak acid pushes the equilibrium to the right so the degree of dissociation increases and more H$^+$ ions are produced meaning pH increases less than expected

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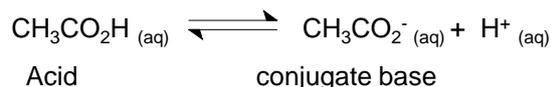
A **basic** buffer solution is made from a weak base and a salt of that weak base (made from reacting the weak base with a strong acid).

Example : ammonia and ammonium chloride NH_3 and $NH_4^+Cl^-$

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 $CH_3CO_2^-Na^+$

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.

The buffer contains a reservoir of HA **and** A $^-$ ions

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.

$$[H^+_{(aq)}] = Ka \frac{[CH_3CO_2H_{(aq)}]}{[CH_3CO_2^-_{(aq)}]}$$

If **small amounts of alkali is added** to the buffer. The OH^- ions will react with H^+ ions to form water.

$H^+ + OH^- \rightarrow H_2O$
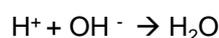
The Equilibrium will then shift to the right to produce more H^+ ions.

$CH_3CO_2H_{(aq)} \rightleftharpoons CH_3CO_2^-_{(aq)} + H^+_{(aq)}$
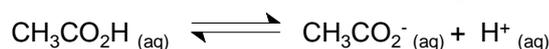
Some ethanoic acid molecules are changed to ethanoate ions but as there is a large concentration of the salt ion in the buffer the ratio $[CH_3CO_2H]/[CH_3CO_2^-]$ stays almost constant, so the pH stays fairly constant.

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

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

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

Normally we rearrange to

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

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

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 salt.

Example 9: making a buffer by adding a salt solution

What would be the pH of a buffer made from 45cm^3 of 0.1M ethanoic acid and 50cm^3 of 0.15 M sodium ethanoate (Ka = 1.7 x 10^{-5}) ?

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

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

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

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

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

Example 10 : making a buffer by adding a solid salt

A buffer solution is made by adding 1.1g of sodium ethanoate into 100 cm^3 of 0.4M ethanoic acid. What is its pH? Ka =1.7 x10^{-5}

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

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

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

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

pH = − log [H$^+$]
= -log 5.07x 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 11 55cm^3 of 0.5M CH$_3$CO$_2$H is reacted with 25cm^3 of 0.35M NaOH. What will be the pH of the resulting buffer solution?

$$CH_3CO_2H + NaOH \rightarrow CH_3CO_2Na + H_2O$$
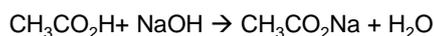
ka is 1.7 x 10^{-5} mol dm^{-3}

Moles CH$_3$CO$_2$H = conc x vol =0.5x 0.055 = 0.0275mol
Moles NaOH = conc x vol = 0.35 x 0.025 = 0.00875

Moles of CH$_3$CO$_2$H in excess = 0.0275-0.00875 = 0.01875 (as 1:1 ratio)

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

$$= 0.01875/ \ 0.08 = 0.234M$$

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

$$= 0.00875/ \ 0.08 = 0.109M$$

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

[H$^+$] = ka x[CH$_3$CO$_2$H] / [CH$_3$CO$_2^-$]

= 1.7 x 10^{-5} x 0.234 / 0.109
= 3.64 x 10^{-5}

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

Buffering action in blood

A carbonic acid– hydrogencarbonate equilibrium acts as a buffer in the control of blood pH
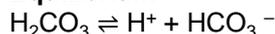
The H$_2$CO$_3$/HCO$_3^-$ buffer is present in blood plasma, maintaining a pH between 7.35 and 7.45.

Equilibrium
$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

Adding alkali reacts with H$^+$ so the above Equilibrium would shift right forming new H$^+$ and more HCO$_3^-$

Buffers can be found naturally in some foods to prevent deterioration due to pH change (caused by bacterial or fungal activity). The pH of the food tends to be acidic which prevents the growth of bacteria. The buffer prevents the pH of the food increasing to a point where bacteria can thrive

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

$$CH_3CO_2^-{}_{(aq)} + H^+ \rightarrow CH_3CO_2H_{(aq)}$$
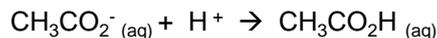
Example 12: 0.005 mol of NaOH is added to 500cm^3 of a buffer where the concentration of ethanoic acid is 0.200 mol dm^{-3} and the concentration of sodium ethanoate is 0.250 mol dm^{-3} . (Ka = 1.7 x 10^{-5})

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 = 0.100mol
Moles sodium ethanoate = conc x vol = 0.25 x 0.500 = 0.125mol

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

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

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

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

pH = − log [H$^+$]
= -log 1.24x 10^{-5}
= 4.91

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
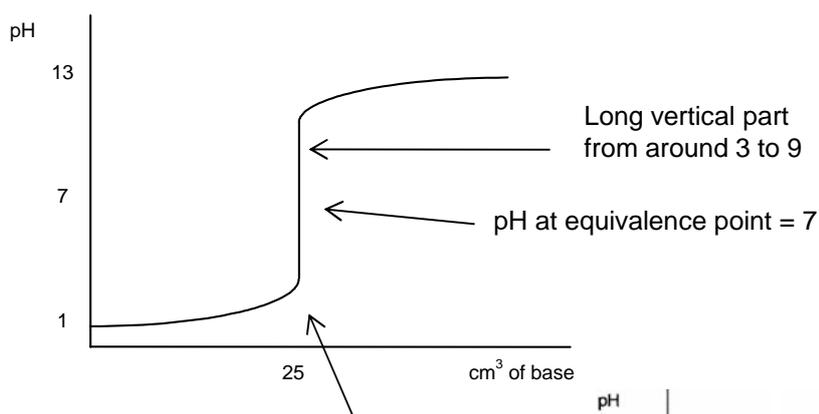7. Add until alkali in excess

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 vertical 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)
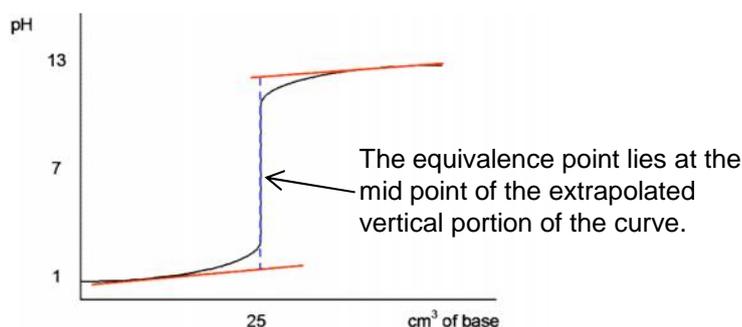
Weak acid – Strong base   e.g. CH$_3$CO$_2$H and NaOH

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

pH starts near 3

Equivalence point >7

Steep part of curve >7 (around 7 to 9)
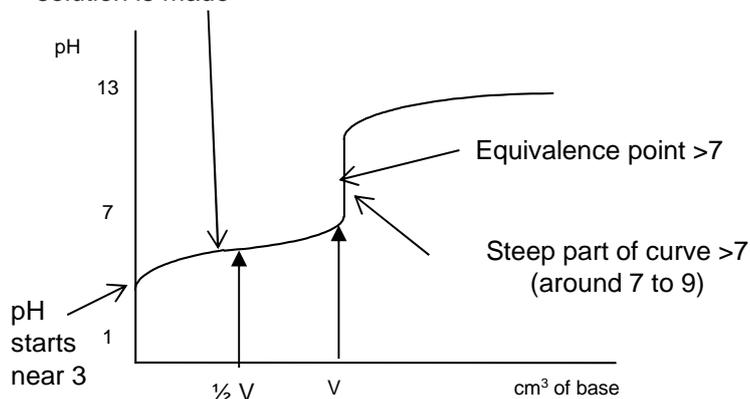
Half neutralisation volume
For weak acids
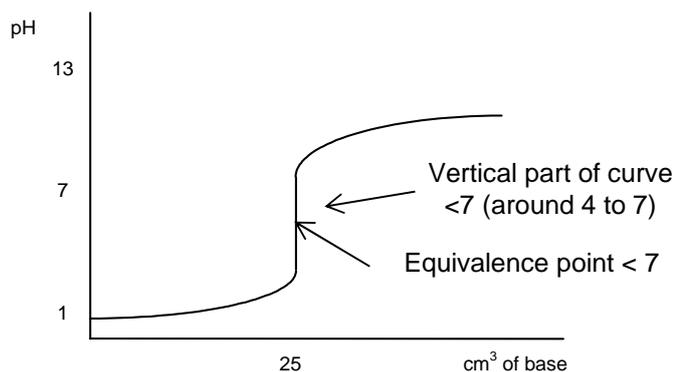
$$Ka = \frac{[H^+_{(aq)}][A^-_{(aq)}]}{[HA_{(aq)}]}$$

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

So Ka = [H$^+$] and pKa = pH

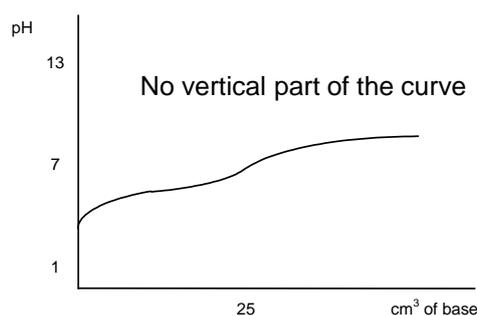If we know the Ka we can then work out the pH at ½ V or vice versa

Strong acid – Weak base   e.g. HCl and NH$_3$

pH

13

7

1

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

Equivalence point < 7

25   cm^3 of base

Weak acid – Weak base   e.g. CH$_3$CO$_2$H and NH$_3$

pH

13   No vertical part of the curve

7

1

25   cm^3 of base

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$^+$ $_{(aq)}$
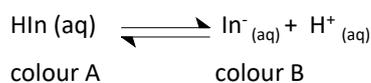
colour A   colour B

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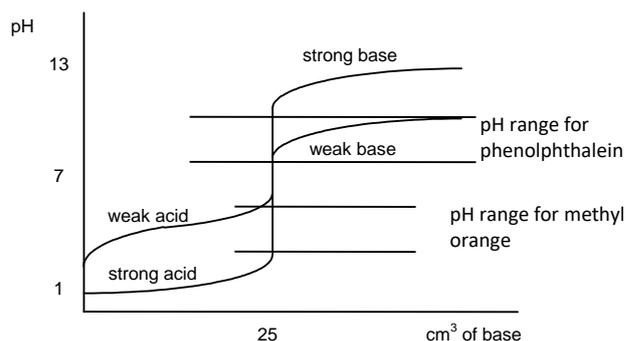
An indicator will work if the pH range of the indicator lies on the steep part of the titration curve. In this case the indicator will change colour rapidly and the colour change will correspond to the neutralisation point.

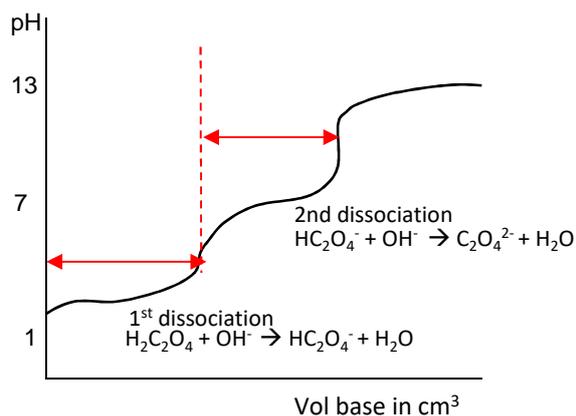Only use phenolphthalein in titrations with strong bases but not weak bases-

Colour change: colourless acid → pink alkali

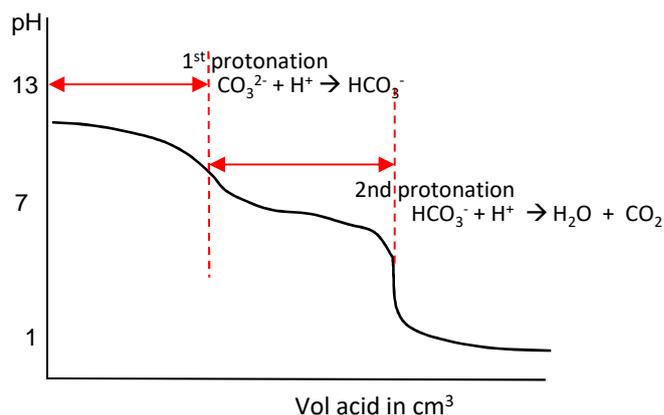Use methyl orange with titrations with strong acids but not weak acids
Colour change: red acid → yellow alkali (orange end point)

pH

13   strong base

7

1

weak base

pH range for phenolphthalein

weak acid

strong acid

pH range for methyl orange

25   cm^3 of base

Diprotic acid with base

pH

$$13$$

$$7$$

$$1$$

2nd dissociation
$HC_2O_4^- + OH^- \rightarrow C_2O_4^{2-} + H_2O$

1st dissociation
$H_2C_2O_4 + OH^- \rightarrow HC_2O_4^- + H_2O$

Vol base in cm³

Diprotic base with acid

pH

$$13$$

$$7$$

$$1$$

1st protonation
$CO_3^{2-} + H^+ \rightarrow HCO_3^-$

2nd protonation
$HCO_3^- + H^+ \rightarrow H_2O + CO_2$

Vol acid in cm³

Diprotic acids will give a two part pH curve with
two end points. Different indicators can be used
to find out the two end points.

Enthalpy change of Neutralisation

The standard enthalpy change of neutralisation is the enthalpy change when solutions of an acid and
an alkali react together under standard conditions to produce 1 mole of water.

Enthalpy changes of neutralisation are always exothermic. For reactions involving strong acids and alkalis, the
values are similar, with values between -56 and -58 kJ mol^{-1} because the same reaction is occurring $H^+ + OH^- \rightarrow$
H_2O

Weak acids have a less exothermic enthalpy change of neutralisation because energy is absorbed to ionise the
acid and break the bond to the hydrogen in the un-dissociated acid.