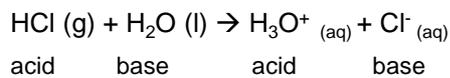


4. Acid Base Equilibria

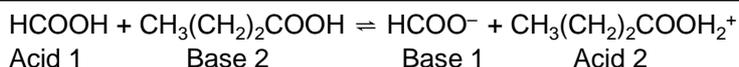
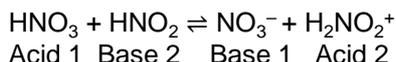
Bronsted-Lowry Definition of acid Base behaviour

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**.



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



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

Calculating pH

$$\text{pH} = -\log [\text{H}^+]$$

Where $[\text{H}^+]$ 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 $[\text{H}^+(\text{aq})]$ 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 $[\text{H}^+]$ from pH

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

On most calculators this is done by pressing

Inv (or 2nd function) \rightarrow log
 \rightarrow - number(pH)

Example 1

What is the concentration of HCl with a pH of 1.35?

$$[\text{H}^+] = 1 \times 10^{-1.35} = 0.045\text{M}$$

Ionic Product for water

In all aqueous solutions and pure water the following equilibrium occurs: $\text{H}_2\text{O (l)} \rightleftharpoons \text{H}^+ \text{ (aq)} + \text{OH}^- \text{ (aq)}$

This equilibrium has the following equilibrium expression

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

Rearrange to

$$K_c \times [\text{H}_2\text{O (l)}] = [\text{H}^+ \text{ (aq)}][\text{OH}^- \text{ (aq)}] \longrightarrow$$

Because $[\text{H}_2\text{O (l)}]$ is much bigger than the concentrations of the ions, we assume its value is constant and make a new constant K_w

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

Learn this expression

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

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

Finding pH of pure water

Pure water/ neutral solutions are **neutral** because the $[H^+_{(aq)}] = [OH^-_{(aq)}]$
 Using $K_w = [H^+_{(aq)}][OH^-_{(aq)}]$ then when neutral $K_w = [H^+_{(aq)}]^2$
 and $[H^+_{(aq)}] = \sqrt{K_w}$
 At 25°C $[H^+_{(aq)}] = \sqrt{1 \times 10^{-14}} = 1 \times 10^{-7}$ so pH = 7

Example 2 : Calculate the pH of water at 50°C given that $K_w = 5.476 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ at 50°C
 $[H^+_{(aq)}] = \sqrt{K_w} = \sqrt{5.476 \times 10^{-14}} = 2.34 \times 10^{-7} \text{ mol dm}^{-3}$
 pH = $-\log 2.34 \times 10^{-7} = 6.6$
 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 K_w expression.

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

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

Assume complete dissociation.

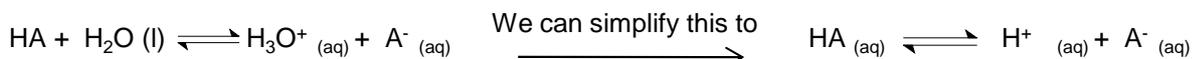
$$K_w = [H^+_{(aq)}][OH^-_{(aq)}] = 1 \times 10^{-14}$$

$$[H^+_{(aq)}] = K_w / [OH^-_{(aq)}] = 1 \times 10^{-14} / 0.1 = 1 \times 10^{-13} \text{ M}$$

$$pH = -\log[1 \times 10^{-13}] = 13.00$$

Weak acids

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



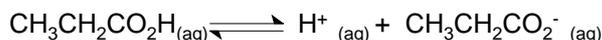
Weak acids dissociation expression

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

The K_a for ethanoic acid is $1.7 \times 10^{-5} \text{ mol dm}^{-3}$.

The larger K_a the stronger the acid

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



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

pKa

Sometimes K_a values are quoted as pKa 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:

- $[H^+_{(aq)}]_{eqm} = [A^-_{(aq)}]_{eqm}$ because they have dissociated according to a 1:1 ratio.
- As the amount of dissociation is small we assume that the initial concentration of the undissociated acid has remained constant.

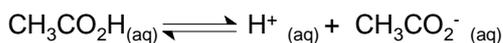
So $[HA_{(aq)}]_{eqm} = [HA_{(aq)}]_{initial}$

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

Simplifies to ↓

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

Example 5 What is the pH of a solution of 0.01M ethanoic acid (K_a is $1.7 \times 10^{-5} \text{ mol dm}^{-3}$)?



$$K_a = \frac{[\text{H}^+_{(\text{aq})}][\text{CH}_3\text{CO}_2^-_{(\text{aq})}]}{[\text{CH}_3\text{CO}_2\text{H}_{(\text{aq})}]} \longrightarrow K_a = \frac{[\text{H}^+_{(\text{aq})}]^2}{[\text{CH}_3\text{CO}_2\text{H}_{(\text{aq})}]_{\text{initial}}} \longrightarrow 1.7 \times 10^{-5} = \frac{[\text{H}^+_{(\text{aq})}]^2}{0.01}$$

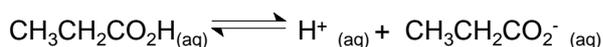
$$[\text{H}^+_{(\text{aq})}]^2 = 1.7 \times 10^{-5} \times 0.01$$

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

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

$$\text{pH} = 3.38$$

Example 6 What is the concentration of propanoic acid with a pH of 3.52 (K_a is $1.35 \times 10^{-5} \text{ mol dm}^{-3}$)?



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

$$K_a = \frac{[\text{H}^+_{(\text{aq})}][\text{CH}_3\text{CH}_2\text{CO}_2^-_{(\text{aq})}]}{[\text{CH}_3\text{CH}_2\text{CO}_2\text{H}_{(\text{aq})}]} \longrightarrow K_a = \frac{[\text{H}^+_{(\text{aq})}]^2}{[\text{CH}_3\text{CH}_2\text{CO}_2\text{H}_{(\text{aq})}]_{\text{initial}}} \longrightarrow 1.35 \times 10^{-5} = \frac{[0.000302]^2}{[\text{CH}_3\text{CH}_2\text{CO}_2\text{H}_{(\text{aq})}]_{\text{initial}}}$$

$$[\text{CH}_3\text{CH}_2\text{CO}_2\text{H}_{(\text{aq})}] = 9.12 \times 10^{-8} / 1.35 \times 10^{-5} \quad [\text{CH}_3\text{CH}_2\text{CO}_2\text{H}_{(\text{aq})}] = 6.75 \times 10^{-3} \text{ M}$$

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.

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]}$$

At half neutralisation we can make the assumption that $[\text{HA}] = [\text{A}^-]$

$$\text{So } [\text{H}^+_{(\text{aq})}] = K_a$$

$$\text{And } \text{pH} = \text{p}K_a$$

Example 7

What is the pH of the resulting solution when **25cm³ of 0.1M NaOH** is added to **50cm³ of 0.1M CH₃COOH** (K_a 1.7×10^{-5})

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

$$\text{pH} = \text{p}K_a = -\log (1.7 \times 10^{-5}) = 4.77$$

Diluting an acid or alkali

pH of diluted strong acid

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

$$\text{pH} = -\log [\text{H}^+]$$

pH of diluted base

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

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

$$\text{pH} = -\log [\text{H}^+]$$

Example 8 Calculate the new pH when 50.0 cm³ of 0.150 mol dm⁻³ HCl is mixed with 500 cm³ of water.

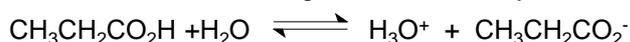
$$[\text{H}^+] = [\text{H}^+]_{\text{old}} \times \frac{\text{old volume}}{\text{new volume}} \quad [\text{H}^+_{(\text{aq})}] = 0.150 \times \frac{0.05}{0.55} \quad [\text{H}^+_{(\text{aq})}] = 0.0136$$

$$\text{pH} = -\log [\text{H}^+] = -\log 0.0136 = 1.87$$

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



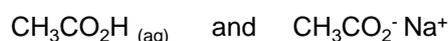
Diluting the weak acid pushes the equilibrium to the right so the degree of dissociation increases and more H⁺ ions are produced meaning pH increases less than expected

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.

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

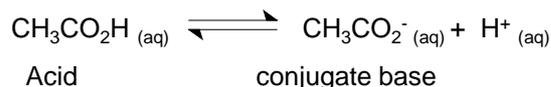


A **basic** buffer solution is made from a weak base and a salt of that weak base (made from reacting the weak base with a strong acid).

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

How Buffer solutions work

In an ethanoic acid buffer



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

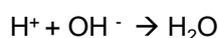
The buffer contains a reservoir of HA and A^- ions

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, $\text{CH}_3\text{CO}_2^-_{(\text{aq})} + \text{H}^+_{(\text{aq})} \rightarrow \text{CH}_3\text{CO}_2\text{H}_{(\text{aq})}$

As there is a large concentration of the salt ion in the buffer the ratio $[\text{CH}_3\text{CO}_2\text{H}]/[\text{CH}_3\text{CO}_2^-]$ stays almost constant, so the pH stays fairly constant.

$$[\text{H}^+_{(\text{aq})}] = K_a \frac{[\text{CH}_3\text{CO}_2\text{H}_{(\text{aq})}]}{[\text{CH}_3\text{CO}_2^-_{(\text{aq})}]}$$

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.



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 $[\text{CH}_3\text{CO}_2\text{H}]/[\text{CH}_3\text{CO}_2^-]$ 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

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

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

Normally we rearrange to \rightarrow

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

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.

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

Example 9: making a buffer by adding a salt solution

What would be the pH of a buffer made from 45cm³ of 0.1M ethanoic acid and 50cm³ of 0.15 M sodium ethanoate ($K_a = 1.7 \times 10^{-5}$) ?

Work out the moles of both solutions

Moles ethanoic = conc x vol = $0.1 \times 0.045 = 0.0045\text{mol}$

Moles sodium ethanoate = conc x vol = $0.15 \times 0.050 = 0.0075$

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

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

$$\begin{aligned} \text{pH} &= -\log [H^+] \\ &= -\log 1.02 \times 10^{-5} \\ &= 4.99 \end{aligned}$$

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

Example 10 : making a buffer by adding a solid salt

A buffer solution is made by adding 1.1g of sodium ethanoate into 100 cm³ of 0.4M ethanoic acid. What is its pH? $K_a = 1.7 \times 10^{-5}$

Work out the moles of both solutions

Moles ethanoic = conc x vol = $0.4 \times 0.1 = 0.04\text{mol}$

Moles sodium ethanoate = mass/Mr = $1.1/82 = 0.0134$

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

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

$$\begin{aligned} \text{pH} &= -\log [H^+] \\ &= -\log 5.07 \times 10^{-5} \\ &= 4.29 \end{aligned}$$

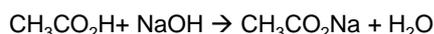
We can enter moles of acid and salt straight into the equation as they both have the same new final volume

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

Example 11 55cm³ of 0.5M CH₃CO₂H is reacted with 25cm³ of 0.35M NaOH. What will be the pH of the resulting buffer solution?

Moles CH₃CO₂H = conc x vol = $0.5 \times 0.055 = 0.0275\text{mol}$

Moles NaOH = conc x vol = $0.35 \times 0.025 = 0.00875$



k_a is $1.7 \times 10^{-5} \text{ mol dm}^{-3}$

Moles of CH₃CO₂H in excess = $0.0275 - 0.00875 = 0.01875$ (as 1:1 ratio)

$$\begin{aligned} [\text{CH}_3\text{CO}_2\text{H}] &= \frac{\text{moles excess CH}_3\text{CO}_2\text{H}}{\text{total volume (dm}^3\text{)}} \\ &= 0.01875 / 0.08 = 0.234\text{M} \end{aligned}$$

$$\begin{aligned} [\text{CH}_3\text{CO}_2^-] &= \frac{\text{moles OH}^- \text{ added}}{\text{total volume (dm}^3\text{)}} \\ &= 0.00875 / 0.08 = 0.109\text{M} \end{aligned}$$

$$k_a = \frac{[H^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]}$$

$$\begin{aligned} [H^+] &= k_a \times [\text{CH}_3\text{CO}_2\text{H}] / [\text{CH}_3\text{CO}_2^-] \\ &= 1.7 \times 10^{-5} \times 0.234 / 0.109 \\ &= 3.64 \times 10^{-5} \end{aligned}$$

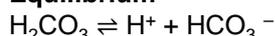
$$\begin{aligned} \text{pH} &= -\log [H^+] \\ &= -\log 3.64 \times 10^{-5} \\ &= 4.44 \end{aligned}$$

Calculating change in pH of buffer on addition of alkali

If a small amount of alkali is added to a buffer then the moles of the 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

Buffering action in blood

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

Equilibrium

The H₂CO₃/HCO₃⁻ buffer is present in blood plasma, maintaining a pH between 7.35 and 7.45.

Adding alkali reacts with H⁺ so the above Equilibrium would shift right forming new H⁺ and more HCO₃⁻

Titration curves

Constructing a PH curve

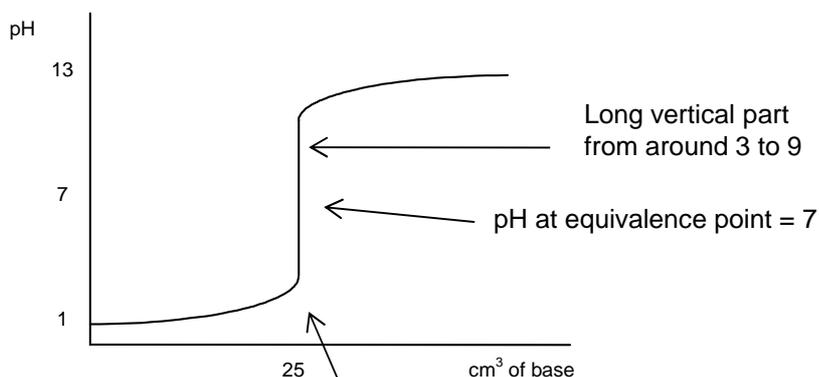
- Measure initial pH of the acid
- Add alkali in small amounts noting the volume added
- Stir mixture to equalise the pH
- Measure and record the pH to 1 dp
- When approaching endpoint add in smaller volumes of alkali
- Add until alkali in excess

Calibrate meter first by measuring known pH of a buffer solution. This is necessary because pH meters can lose accuracy on storage

Can improve accuracy by **maintaining** constant temperature

Strong acid – Strong base

e.g. HCl and NaOH

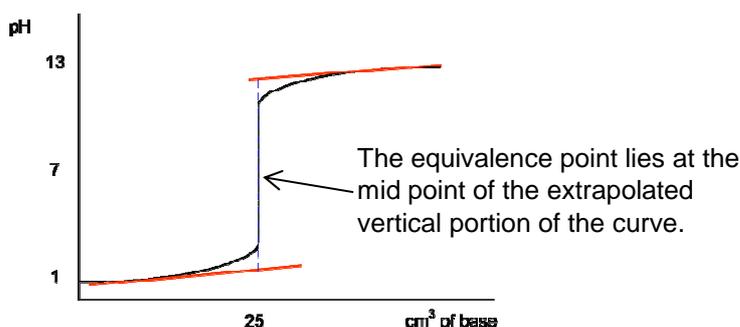


You may also have to work out the neutralisation volume from titration data given in the question. These are done by standard titration calculations from module 1.

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

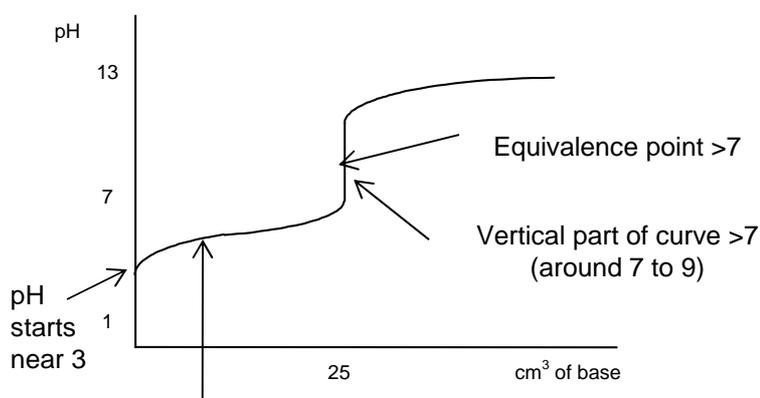
There are 4 main types of curve

1. Strong acid and strong base
2. Weak acid and strong base
3. Strong acid and weak base
4. Weak acid and weak base



Weak acid – Strong base

e.g. CH₃CO₂H 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

Half neutralisation volume

For weak acids

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

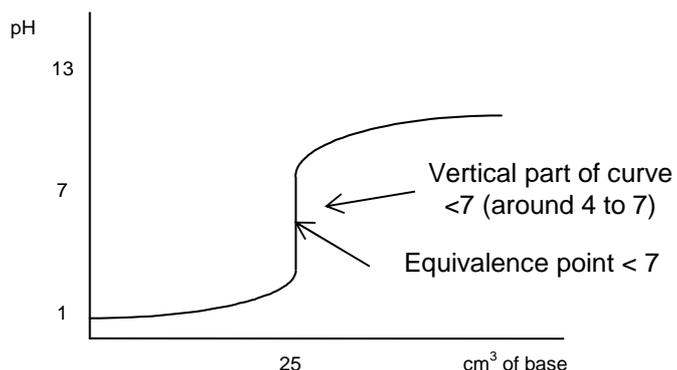
At $\frac{1}{2}$ the neutralisation volume the $[HA] = [A^-]$

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

If we know the K_a we can then work out the pH at $\frac{1}{2} V$ or vice versa

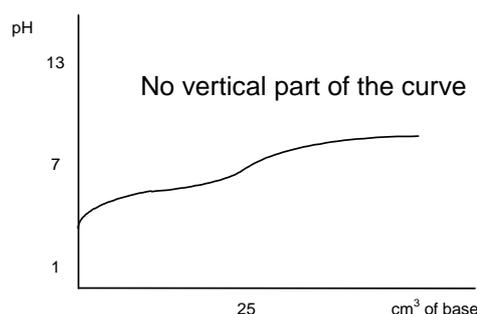
Strong acid – Weak base

e.g. HCl and NH₃



Weak acid – Weak base

e.g. CH₃CO₂H and NH₃

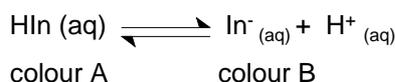


Choosing an Indicator

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 a different ranges

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



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 vertical 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)

