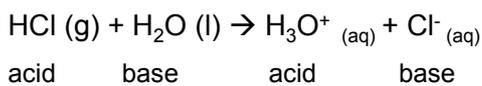


3. Acid Base Equilibria

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.

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

Rearrange to

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

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

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

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

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 $[\text{H}^+(\text{aq})] = [\text{OH}^-(\text{aq})]$. So if $K_w = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})]$ then when neutral if $K_w = [\text{H}^+(\text{aq})]^2$ and $[\text{H}^+(\text{aq})] = \sqrt{K_w}$. At 25°C $[\text{H}^+(\text{aq})] = \sqrt{1 \times 10^{-14}} = 1 \times 10^{-7}$ so pH = 7

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

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

$$[\text{H}^+(\text{aq})] = \sqrt{K_w} = \sqrt{5.476 \times 10^{-14}} = 2.34 \times 10^{-7} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log 2.34 \times 10^{-7} = \mathbf{6.6}$$

It is still neutral though as $[\text{H}^+(\text{aq})] = [\text{OH}^-(\text{aq})]$

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.

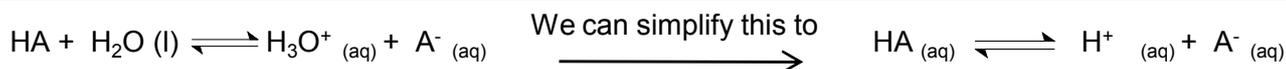
$$K_w = [H^+(aq)][OH^-(aq)] = 1 \times 10^{-14}$$

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

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

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 equation for dissociation of propanoic acid and its K_a expression



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

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.

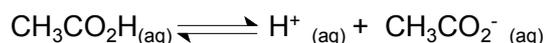
So $[HA(aq)]_{eqm} = [HA(aq)]_{initial}$

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

Simplifies to \downarrow

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

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



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

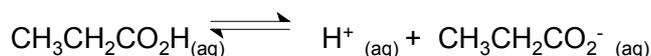
$$[H^+(aq)]^2 = 1.7 \times 10^{-5} \times 0.01$$

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

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

$$pH = 3.38$$

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



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

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

$$[CH_3CO_2H_{(aq)}] = 9.12 \times 10^{-8} / 1.35 \times 10^{-5}$$

$$[CH_3CO_2H_{(aq)}] = 6.75 \times 10^{-3} \text{ M}$$

pH Calculations involving neutralisation reactions

These can be quite complex calculations working out the pH of a partially neutralised acid or the pH of the solution if too much alkali has been added and has gone past neutralisation. The method differs if the acid is strong or weak for the partially neutralised case.

Strong acid and Strong base neutralisations

Work out moles of original acid
Work out moles of base added
Work out which one is in excess

If excess acid

Work out new concentration of excess H⁺ ions

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

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

Total volume =
vol of acid + vol
of base added

If excess alkali

Work out new concentration of excess OH⁻ ions

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

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

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

Total volume =
vol of acid + vol
of base added

Example 7 15cm³ of 0.5M HCl is reacted with 35cm³ of 0.55M NaOH. What will be the pH of the resulting mixture?

Moles HCl = conc x vol = 0.5 x 0.015 = 0.0075mol

Moles NaOH = conc x vol = 0.55 x 0.035 = 0.01925

HCl + NaOH → NaCl + H₂O

Moles of NaOH in excess = 0.01925 - 0.0075 = 0.01175 (as 1:1 ratio)

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

$$= 0.01175 / 0.05 = 0.235\text{M}$$

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

$$= 1 \times 10^{-14} / 0.235 = 4.25 \times 10^{-14}$$

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

$$= -\log 4.25 \times 10^{-14}$$

$$= 13.37$$

Example 8 45cm³ of 1M HCl is reacted with 30cm³ of 0.65M NaOH. What will be the pH of the resulting mixture?

Moles HCl = conc x vol = 1 x 0.045 = 0.045mol

Moles NaOH = conc x vol = 0.65 x 0.030 = 0.0195

HCl + NaOH → NaCl + H₂O

Moles of HCl in excess = 0.045 - 0.0195 = 0.0255 (as 1:1 ratio)

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

$$= 0.0255 / 0.075 = 0.34\text{M}$$

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

$$= -\log 0.34$$

$$= 0.47$$

Weak acid and Strong base neutralisations

Work out moles of original acid
Work out moles of base added
Work out which one is in excess

If excess acid

Work out new concentration of excess HA

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

Work out concentration of salt formed [A⁻]

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

Rearrange $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$ to get [H⁺]

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

If excess alkali use the same method with excess alkali and strong acid above

Example 9 55cm³ of 0.5M CH₃CO₂H is reacted with 25cm³ of 0.35M NaOH. What will be the pH of the resulting mixture?

Moles CH₃CO₂H = conc x vol = 0.5 x 0.055 = 0.0275mol

Moles NaOH = conc x vol = 0.35 x 0.025 = 0.00875

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

$$[\text{CH}_3\text{CO}_2\text{H}] = \frac{\text{moles excess CH}_3\text{CO}_2\text{H}}{\text{total volume (dm}^3\text{)}}$$

$$= 0.01875 / 0.08 = 0.234\text{M}$$

$$[\text{CH}_3\text{CO}_2^-] = \frac{\text{moles OH}^- \text{ added}}{\text{total volume (dm}^3\text{)}}$$

$$= 0.00875 / 0.08 = 0.109\text{M}$$

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

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

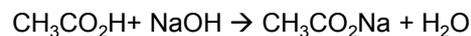
$$= 1.7 \times 10^{-5} \times 0.243 / 0.109$$

$$= 3.79 \times 10^{-3}$$

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

$$= -\log 3.79 \times 10^{-3}$$

$$= 4.42$$



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

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

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

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

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

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

Example 10

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

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

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

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

pH of diluted base

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

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

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

Example 11 Calculate the new pH when 50.0 cm³ of 0.150 mol dm⁻³ HCl is mixed with 500 cm³ of water.

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

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

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

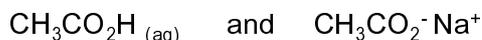
$$\begin{aligned} \text{pH} &= -\log [H^+] \\ &= -\log 0.0136 \\ &= 1.87 \end{aligned}$$

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



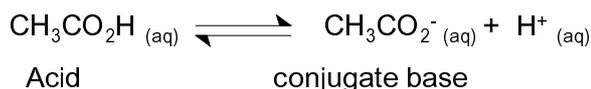
A **basic** buffer solution is made from a weak base and a salt of that weak base (made from reacting the weak base with a strong acid)

Example : ammonia and ammonium chloride



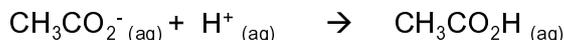
How Buffer solutions work

In an ethanoic acid buffer



In a buffer solution there is a much higher concentration of the salt CH₃CO₂⁻ ion than in the pure acid.

If **small amounts of acid is added** to the buffer: Then Equilibrium will shift to the left removing nearly all the H⁺ ions added, 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)



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

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

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 12: 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 x 0.045 = 0.0045mol

Moles sodium ethanoate = conc x vol = 0.15 x 0.050 = 0.0075

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

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

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

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

Example 13 : 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 x 0.1 = 0.04mol

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

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

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

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

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

If a buffer is made by adding sodium hydroxide to partially neutralise a weak acid then follow the method above for neutralising a weak acid with a strong base (example 9) or possibly the half neutralisation short cut (example 10)

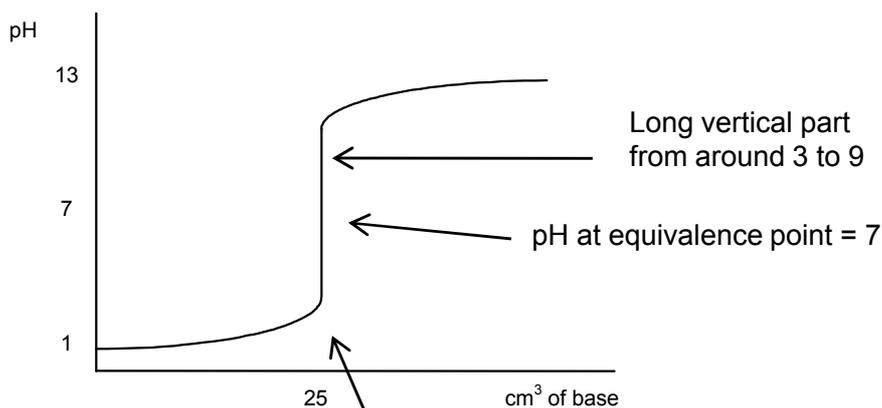
Calculating change in pH of buffer on addition of alkali

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

Titration curves

Strong acid – Strong base

e.g. HCl and NaOH

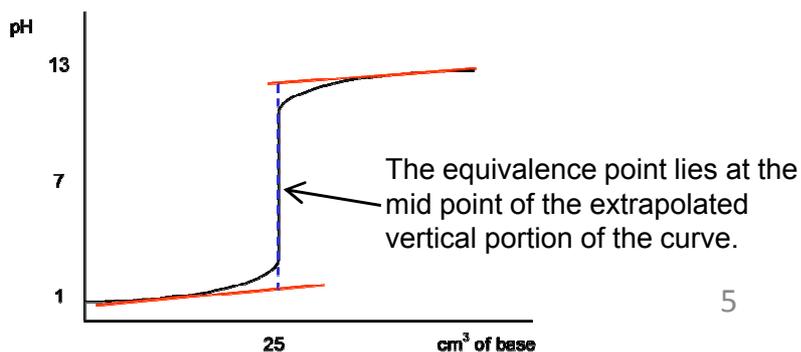


You may also have to work out the neutralisation volume from titration data given in the question. These are done by standard titration calculations from module 1.

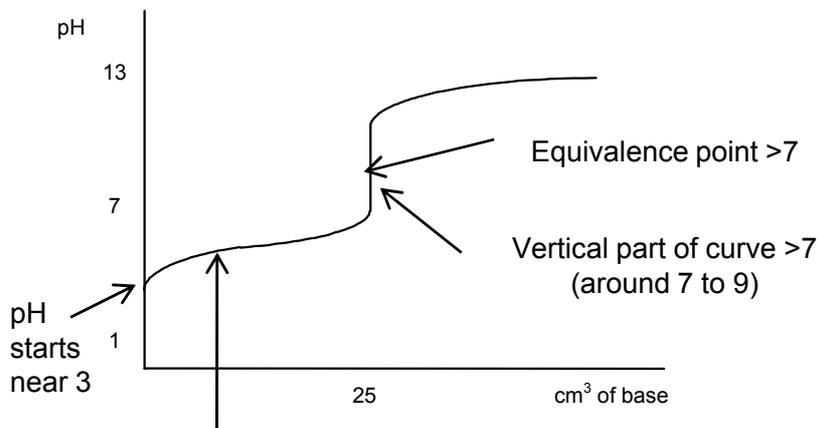
The Key points to sketching a curve:
Initial and final pH
Volume at neutralisation
General Shape (pH at neutralisation)

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. $\text{CH}_3\text{CO}_2\text{H}$ 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

Half neutralisation volume

For weak acids

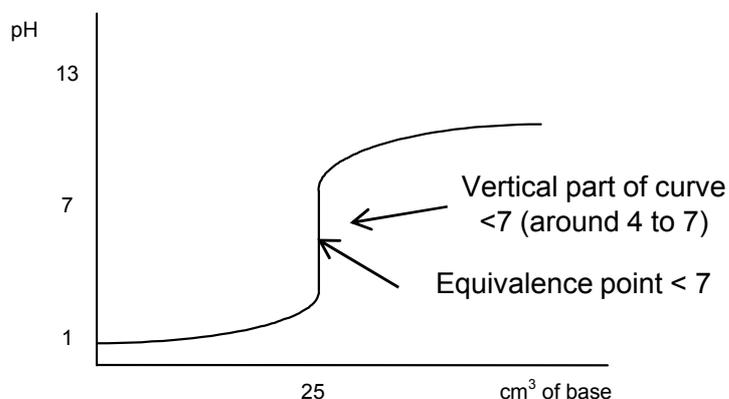
$$K_a = \frac{[\text{H}^+_{(aq)}][\text{A}^-_{(aq)}]}{[\text{HA}_{(aq)}]}$$

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

So $K_a = [\text{H}^+]$ and $\text{p}K_a = \text{pH}$

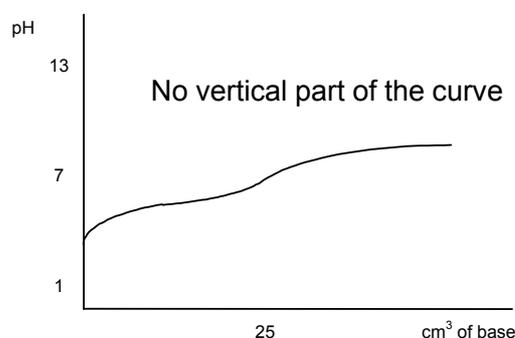
If we know the K_a we can then work out the pH at $\frac{1}{2} V$ or vice versa

Strong acid – Weak base e.g. HCl and NH_3



Weak acid – Weak base

e.g. $\text{CH}_3\text{CO}_2\text{H}$ and NH_3

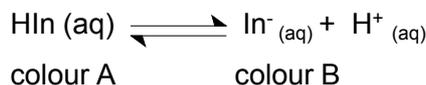


Choosing an Indicator

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 $[\text{HIn}] = [\text{In}^-]$. 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

Use methyl orange with titrations with strong acids but not weak acids

