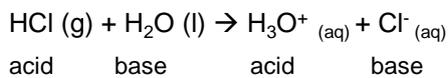


4. 35 Acid Base Equilibria

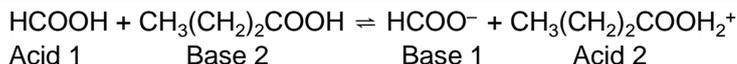
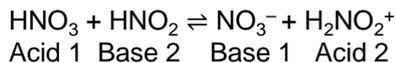
Bronsted-Lowry Definition of acid Base behaviour

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: $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$

This equilibrium has the following equilibrium expression

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

Rearrange to

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

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

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

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

Using $K_w = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})]$ then when neutral $K_w = [\text{H}^+(\text{aq})]^2$
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

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

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 $[\text{H}^+(\text{aq})]$ using the K_w expression.

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

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

Assume complete dissociation.

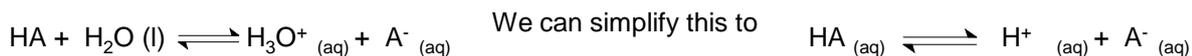
$$K_w = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})] = 1 \times 10^{-14}$$

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

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

Weak acids

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



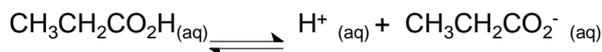
Weak acids dissociation expression

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

pKa

Sometimes K_a values are quoted as pKa values
 $\text{pKa} = -\log K_a$ so $K_a = 10^{-\text{pKa}}$

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



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

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

The larger K_a the stronger the acid

Calculating pH of a weak acid

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

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

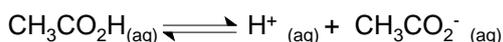
So $[\text{HA} (\text{aq})]_{\text{eqm}} = [\text{HA} (\text{aq})]_{\text{initial}}$

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

Simplifies to \downarrow

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

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



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

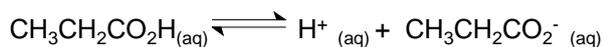
$$[\text{H}^+ (\text{aq})]^2 = 1.7 \times 10^{-5} \times 0.01$$

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

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

$$\text{pH} = 3.38$$

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



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

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

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

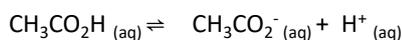
Name	Equation with conjugate base	Ka mol dm ⁻³ .	Pka
Hydrofluoric	$\text{HF}_{(\text{aq})} \rightleftharpoons \text{F}^{-}_{(\text{aq})} + \text{H}^{+}_{(\text{aq})}$	5.60×10^{-4}	3.25
Ethanoic acid	$\text{CH}_3\text{CO}_2\text{H}_{(\text{aq})} \rightleftharpoons \text{CH}_3\text{CO}_2^{-}_{(\text{aq})} + \text{H}^{+}_{(\text{aq})}$	1.7×10^{-5}	4.75
Hydrocyanic acid	$\text{HCN}_{(\text{aq})} \rightleftharpoons \text{CN}^{-}_{(\text{aq})} + \text{H}^{+}_{(\text{aq})}$	4.9×10^{-10}	9.31

The larger the value of Ka the smaller the value of pKa

The stronger the acid the smaller the value of pKa

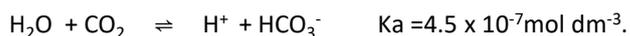
Why do some acids react with sodium carbonate to give CO₂ ?

Ethanoic acid will react with sodium carbonate



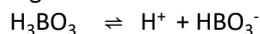
The H⁺ ions produced in this reaction force the following equilibria in the box below involving carbonate ions to the left (by le Chatelier), producing CO₂

Carbonate Equilibria



However if the acid is a weaker acid than carbonic i.e. has a ka < 4.5 x 10⁻⁷ mol dm⁻³ then it will not be able to donate protons to the carbonic acid and no CO₂ will be produced.

E.g. Boric acid has a ka of 5.8 x 10⁻¹⁰ mol dm⁻³ and does not react with sodium carbonate.



Trichloroethanoic acid	2.3 x 10 ⁻¹	↓ Decreasing acid strength ↓ Acids below carbonic acid will not give off CO ₂ with sodium carbonate
Dichloroethanoic acid	5.0 x 10 ⁻²	
Chloroethanoic acid	1.3 x 10 ⁻³	
Benzoic acid	6.3 x 10 ⁻⁵	
Ethanoic acid	1.7 x 10 ⁻⁵	
Carbonic acid	4.5 x 10 ⁻⁷	
Boric acid	5.8 x 10 ⁻¹⁰	
Phenol	1.28 x 10 ⁻¹⁰	

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

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

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

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

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

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

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

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

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

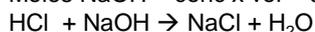
$$\text{pH} = -\log [\text{H}^+]$$

Total volume =
vol of acid + vol
of base added

Example 8 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



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

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

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

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

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

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

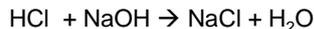
$$= -\log 4.25 \times 10^{-14}$$

$$= 13.37$$

Example 9 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



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 10 55cm³ of 0.5M CH₃CO₂H is reacted with 25cm³ of 0.35M NaOH. What will be the pH of the resulting mixture?

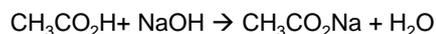
Moles CH₃CO₂H = conc x vol = 0.5 x 0.055 = 0.0275mol

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)

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

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



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

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

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

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

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

$$= 1.7 \times 10^{-5} \times 0.234 / 0.109$$

$$= 3.64 \times 10^{-5}$$

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

$$= -\log 3.64 \times 10^{-5}$$

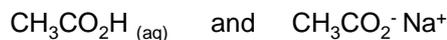
$$= 4.44$$

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

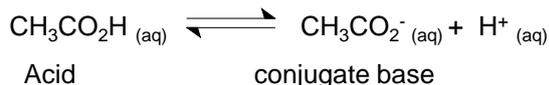


A **basic** buffer solution is made from a weak base and a salt of that weak base (made from reacting the weak base with a strong acid).

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.

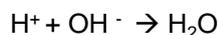
The buffer contains a reservoir of HA and A^- ions

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 11: 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 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

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

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

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

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

Example 12 : 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 x 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

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

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

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

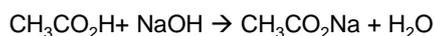
We can enter moles of acid and salt straight into the equation as they both have the same new final volume

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

Example 13 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 x 0.055 = 0.0275mol

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



k_a is 1.7 x 10⁻⁵ mol dm⁻³

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

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

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

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

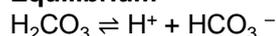
$$\begin{aligned} [H^+] &= k_a \times [\text{CH}_3\text{CO}_2\text{H}] / [\text{CH}_3\text{CO}_2^-] \\ &= 1.7 \times 10^{-5} \times 0.234 / 0.109 \\ &= 3.64 \times 10^{-5} \end{aligned}$$

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

Buffering action in blood

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

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

Equilibrium

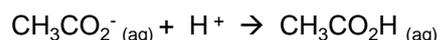
Adding alkali reacts with H⁺ so the above Equilibrium would shift right forming new H⁺ and more HCO₃⁻

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.



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.



Example 14: 0.005 mol of NaOH is added to 500cm³ 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. ($K_a = 1.7 \times 10^{-5}$)

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

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

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

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

$$[\text{H}^+_{(\text{aq})}] = 1.24 \times 10^{-5}$$

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

Required activity 9: Titration curves

Constructing a pH curve

1. Transfer 25cm³ 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 (2cm³) 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

There are 4 main types of curve

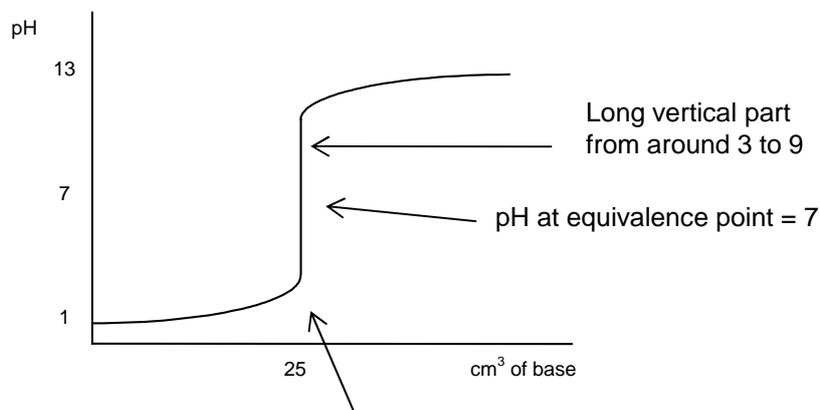
1. Strong acid and strong base
2. Weak acid and strong base
3. Strong acid and weak base
4. Weak acid and weak base

The Key points to sketching a curve:

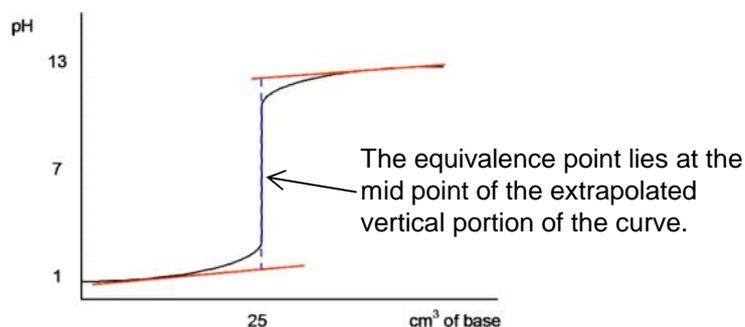
- Initial and final pH
- Volume at neutralisation
- General Shape (pH at neutralisation)

Strong acid – Strong base

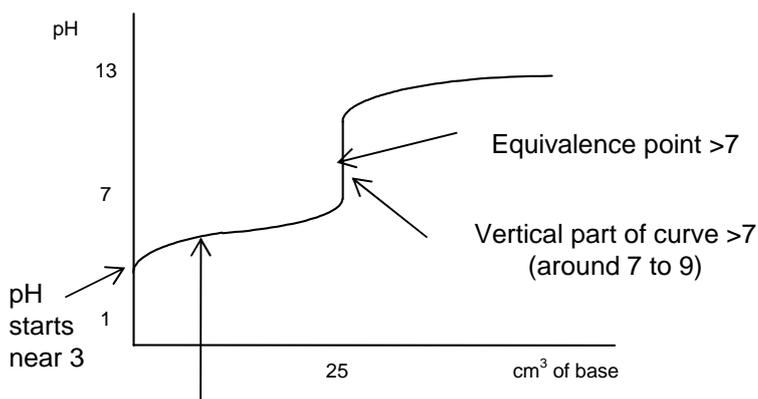
e.g. HCl and NaOH



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



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

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

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

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 $[\text{HA}] = [\text{A}^-]$

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

And **pH = pka**

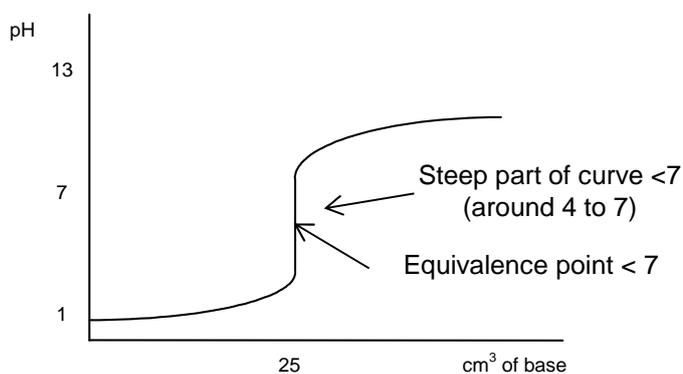
Example 15

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)

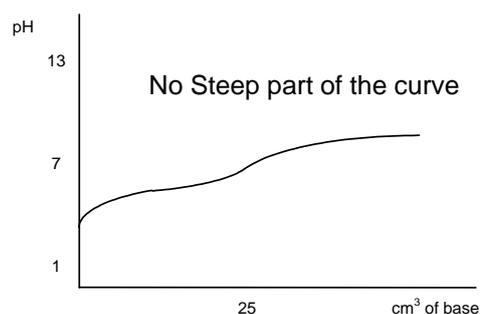
pH = pka = $-\log(1.7 \times 10^{-5}) = 4.77$

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

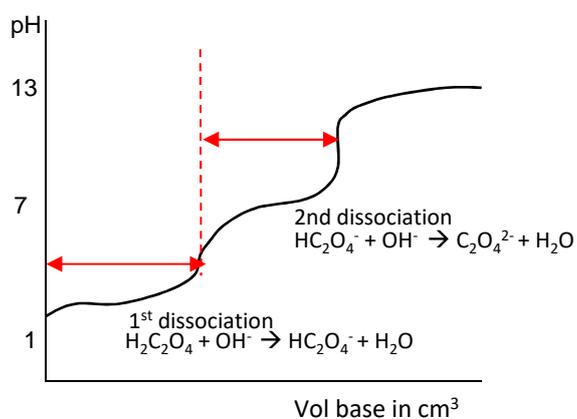


Weak acid – Weak base

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

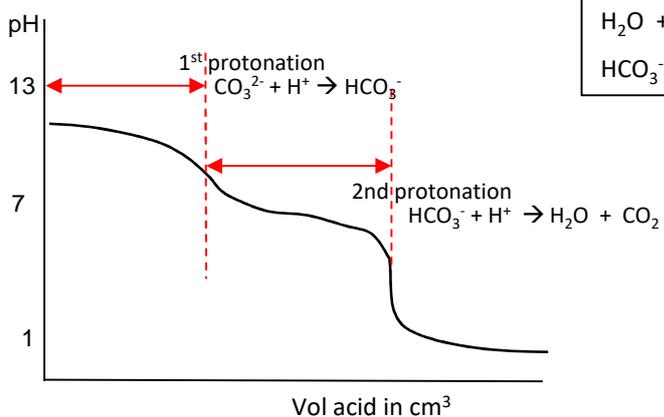


Diprotic acid with base

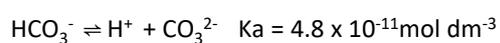
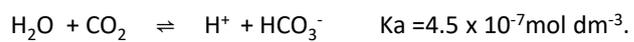


Diprotic acids will give a two part pH curve with two end points. Different indicators can be used to find out the two end points.

Diprotic base with acid



Carbonate Equilibria



Choosing an Indicator

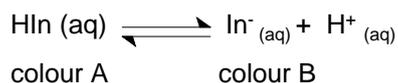
Indicators can be considered as weak acids. The acid must have a different colour to its conjugate base

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 $[\text{HIn}] = [\text{In}^-]$. To choose a correct indicator for a titration one should pick an indicator whose end-point coincides with the equivalence point for the titration.

How indicators work



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.

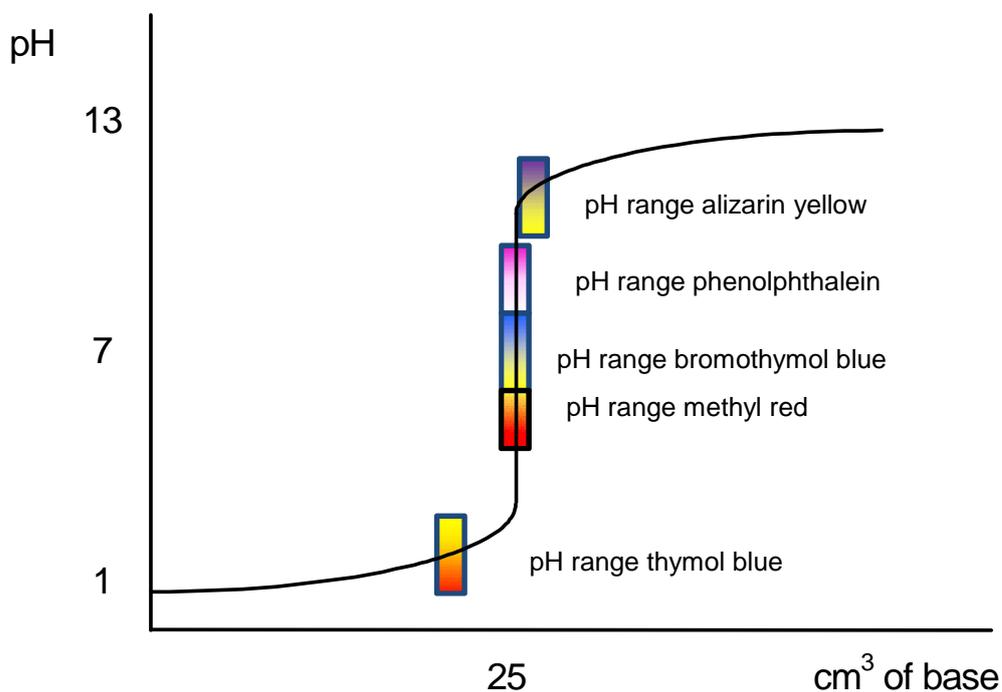
An indicator will work if the pH range of the indicator lies on the **steep** part of the titration curve. In this case the indicator will change colour rapidly and the colour change will correspond to the neutralisation point.

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

Colour change: colourless acid \rightarrow pink alkali

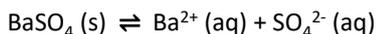
Use methyl orange with titrations with strong acids but not weak acids

Colour change: red acid \rightarrow yellow alkali (orange end point)



Solubility Product

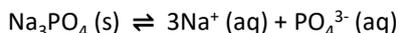
Consider the dissolving of a solid in water as an equilibrium



An equilibrium expression can be written for the reaction

$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

Note the case where multiple ions are dissociated



$$K_{\text{sp}} = [\text{Na}^+]^3[\text{PO}_4^{3-}]$$

Note the $\text{BaSO}_4(\text{s})$ does not appear in the expression. In a heterogeneous equilibrium, concentration terms for solids are not included because they are constant

The value of K_{sp} corresponds to the case where it is a **saturated solution** (i.e. the maximum amount of solute that can be dissolved in a solvent)

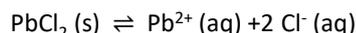
Unit of K_{sp}

Like other equilibrium constants the unit of K_{sp} will vary depending on the expression.

$$\begin{aligned} K_{\text{sp}} &= [\text{Na}^+]^3 [\text{PO}_4^{3-}] \\ &= [\text{mol dm}^{-3}]^3 [\text{mol dm}^{-3}] \\ &= \text{mol}^4 \text{dm}^{-12} \end{aligned}$$

Example 17

A saturated solution of PbCl_2 has the concentration of $[\text{PbCl}_2(\text{aq})]$ of $3.5 \times 10^{-2} \text{ mol dm}^{-3}$. Calculate the K_{sp} for this solution.



if $[\text{PbCl}_2] = 3.5 \times 10^{-2}$ then $[\text{Pb}^{2+}] = 3.5 \times 10^{-2}$ and $[\text{Cl}^-] = 7.0 \times 10^{-2}$

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Cl}^-]^2$$

$$\begin{aligned} K_{\text{sp}} &= (3.5 \times 10^{-2}) \times (7.0 \times 10^{-2})^2 \\ &= 1.715 \times 10^{-4} \text{ mol}^3 \text{ dm}^{-9} \end{aligned}$$

Example 18

The K_{sp} for silver phosphate, Ag_3PO_4 , is 1.25×10^{-20} . Calculate $[\text{Ag}^+(\text{aq})]$ in a saturated solution of Ag_3PO_4 .

$$K_{\text{sp}} = [\text{Ag}^+]^3 [\text{PO}_4^{3-}]$$

make $[\text{PO}_4^{3-}] = y$ and therefore $[\text{Ag}^+] = 3y$

$$K_{\text{sp}} = [3y]^3 [y] = 27y^4$$

$$y = (K_{\text{sp}} / 27)^{1/4}$$

$$y = (1.25 \times 10^{-20} / 27)^{1/4} = 4.64 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\begin{aligned} [\text{Ag}^+] &= 3y \\ &= 1.39 \times 10^{-5} \text{ mol dm}^{-3} \end{aligned}$$

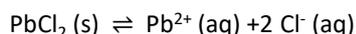
Case where concentrations are less than those of a saturated solution

If the ionic concentrations, put into the K_{sp} expression, give a value less than the solubility product, then the solution is not saturated. No solid precipitate would be seen

Common Ion Effect

If a mixture of salts present has an ion in common then they will have an effect on each other's solubility.

If sodium chloride solution is added to a solution of lead chloride then the increased concentration of chloride ions will shift the lead chloride equilibrium to the left



The solubility of the lead chloride would therefore decrease and more solid would be produced

The solubility of $\text{Ca}(\text{OH})_2$ in $0.1 \text{ mol dm}^{-3} \text{ NaOH}$ is lower than that in water.

It is less soluble in NaOH due to the common hydroxide ion effect. It causes the equilibrium $\text{Ca}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$

to be shifted to the left by the higher hydroxide ion concentration