

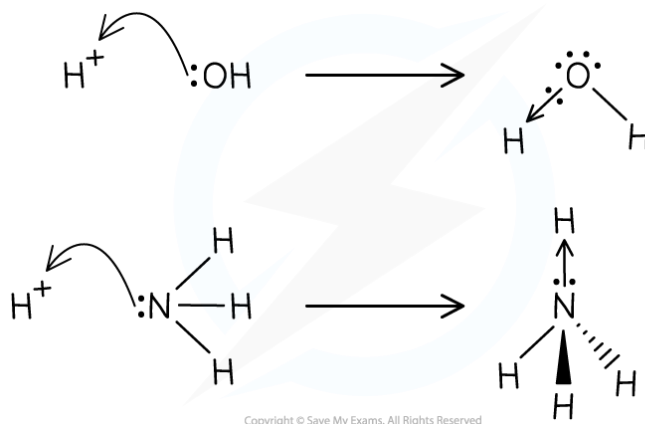
# Lewis Theory of Acids & Bases

- A more general definition of acids and bases was given by G.N. Lewis who defined them as:
  - A Lewis acid is an electron pair acceptor
  - A Lewis base is an electron pair donor



*General mechanism for Lewis acids and bases*

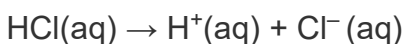
- This enabled a wider range of substances to be classed as acids or bases
- This can be shown in the following examples in which a hydroxide ion, OH<sup>-</sup>, and ammonia, NH<sub>3</sub>, donate a pair of electrons to a hydrogen ion



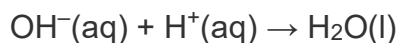
*The OH<sup>-</sup> ion and ammonia act as Lewis bases in both examples by donating an electron pair*

## Brønsted-Lowry Acids and Bases

- A Brønsted-Lowry acid is a species that can donate a proton
  - For example, hydrogen chloride (HCl) is a Brønsted-Lowry acid as it can lose a proton to form a hydrogen (H<sup>+</sup>) and chloride (Cl<sup>-</sup>) ion



- A Brønsted-Lowry base is a species that can accept a proton
  - For example, a hydroxide (OH<sup>-</sup>) ion is a Brønsted-Lowry base as it can accept a proton to form water



Weak acids dissociating

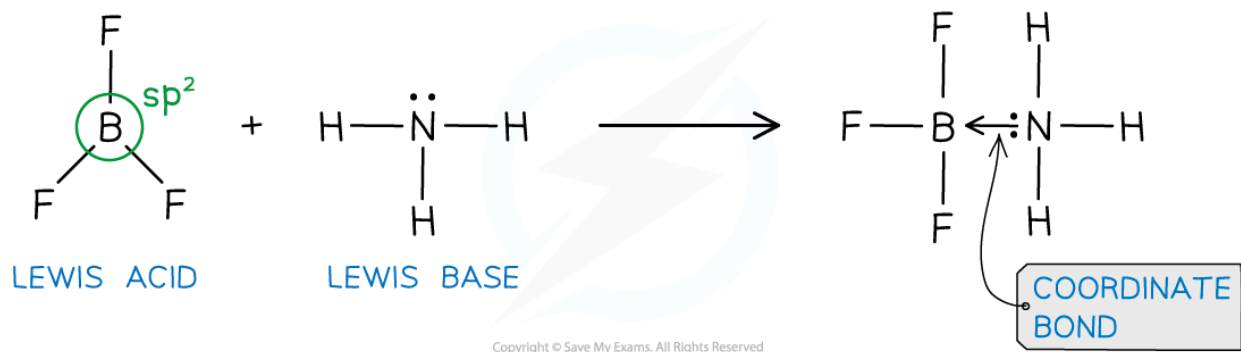
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- In an equilibrium reaction, the products are formed at the same rate as the reactants are used
- This means that at equilibrium, both reactants and products are present in the solution
- For example, ethanoic acid ( $\text{CH}_3\text{COOH}$ ) is a weak acid that partially dissociates in solution
- When equilibrium is established there are  $\text{CH}_3\text{COOH}$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{COO}^-$  and  $\text{H}_3\text{O}^+$  ions present in the solution

### Lewis Acid, Lewis Base, Brønsted-Lowry acid or Brønsted-Lowry base

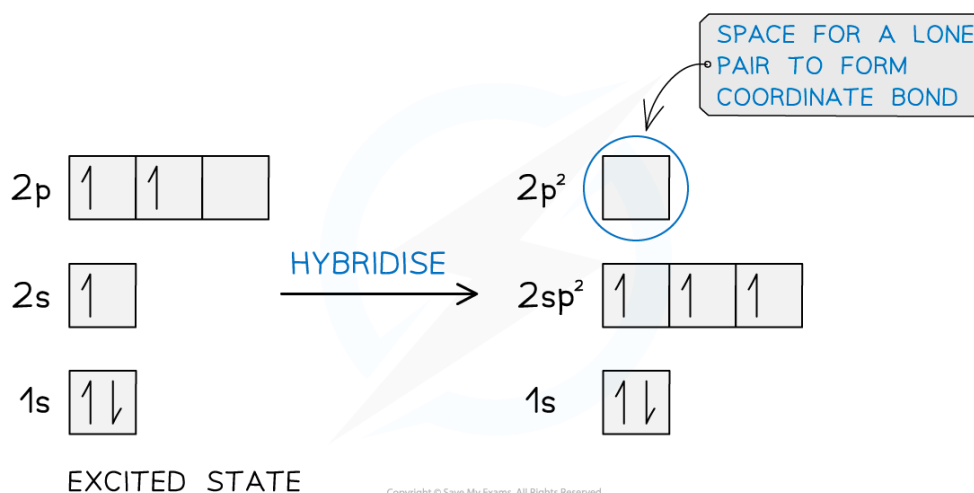
A point to consider when thinking about Lewis acids and bases as well as Brønsted-Lowry acids and bases is the donating and accepting of protons

- Brønsted-Lowry acid and base theory considers acids as proton donors only
- This does not of course occur in every reaction
- For example:
  - The lone pair on the nitrogen atom in ammonia,  $\text{NH}_3$ , can be donated to the boron atom in boron trifluoride,  $\text{BF}_3$ , creating a molecule of  $\text{NH}_3\text{BF}_3$
  - In this case, neither compound reacts as an Brønsted-Lowry acid or Brønsted-Lowry base as no protons ( $\text{H}^+$  ions) are being donated or accepted
  - Only electron pairs are being donated and accepted



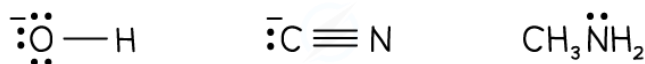
*Ammonia donates a lone pair of electrons to form a coordinate bond*

- Here boron forms three  $\text{sp}^2$  hybridised orbitals leaving a vacant  $2p_z$  orbital which allows the lone pair on the nitrogen atom to form a dative covalent bond



### Hybridisation of the boron atom

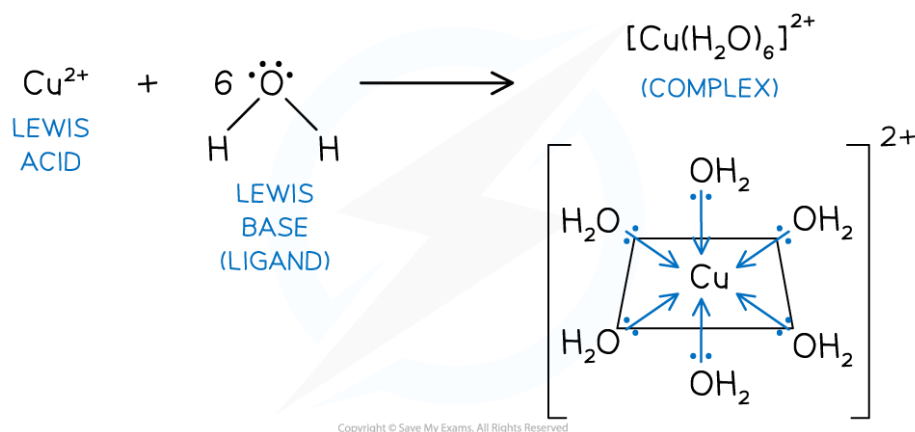
- The following molecules can behave as either Lewis bases and Brønsted-Lowry bases
  - Lewis bases as they can donate an electron pair
  - Brønsted-Lowry base as they can accept a proton



Examples of molecules that can behave both as Lewis bases and Brønsted-Lowry base

## Identifying Lewis Acids & Bases

- In the case of a complex ion, such as hexaaquacopper(II), the water molecule is acting as a Lewis base and the metal ion is acting as a Lewis acid
  - Copper(II), like other transition metals, can form a complex due to a partially occupied d subshell
  - $\text{Cu}^{2+}(\text{aq}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow [\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$

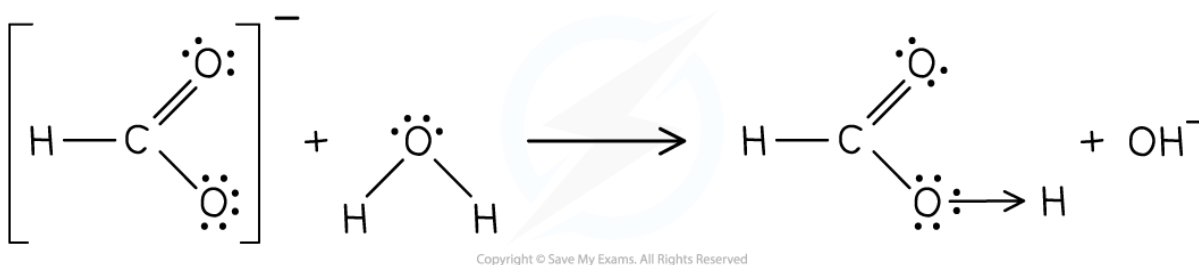


Hexaaquacopper(II) complex

- Given that Lewis acids can accept a pair of electrons, they can be classed as electrophiles
  - An electrophile is a electron-deficient species that can accept a lone pair from a nucleophile, in the same way the  $\text{Cu}^{2+}$  ion accepts electron pairs from water
- The cyanide ion,  $\text{CN}^-$ , water,  $\text{H}_2\text{O}$ , ammonia,  $\text{NH}_3$ , are examples of Lewis bases and they can also act as nucleophiles
  - Nucleophiles are electron rich species with at least one pair of lone electrons

### Worked example

Identify the Lewis acid and Lewis base in the following reaction



*Methanoate ion reacting with water*

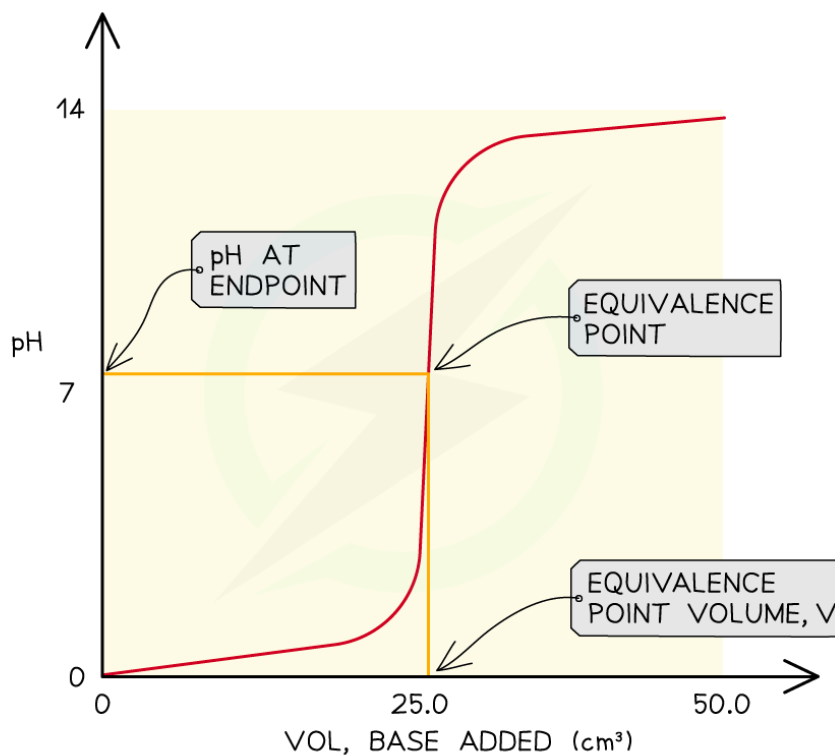
Answer

- The Lewis acid is water,  $\text{H}_2\text{O}$ 
  - The hydrogen in the water molecule is accepting a pair of electrons leaving an  $\text{OH}^-$  ion
- The Lewis base is the methanoate ion,  $\text{HCOO}^-$ 
  - The lone pair of electrons in the methanoate ion forms a coordinate bond with one of the hydrogens from the water molecule

We have seen previously that water can act as a Brønsted-Lowry acid or base, so it should be no surprise that water can act as both a Lewis acid or base depending on how it is interacting with other species

## pH Curves

- During a titration, a pH meter can be used and a pH curve plotted
- A pH curve is a graph showing how the pH of a solution changes as the acid (or base) is added



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### *The features of a pH curve*

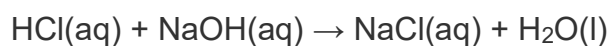
- All pH curves show an s-shape curve
- pH curves yield useful information about how the acid and alkali react together with stoichiometric information
- The midpoint of the inflection is called the equivalence or stoichiometric point
- From the curves you can:
  - Determine the pH of the acid by looking where the curve starts on the y-axis
  - Find the pH at the equivalence point
  - Find volume of base at the equivalence point
  - Obtain the range of pH at the vertical section of the curve

### **Four Types of Acid-Base Titrations**

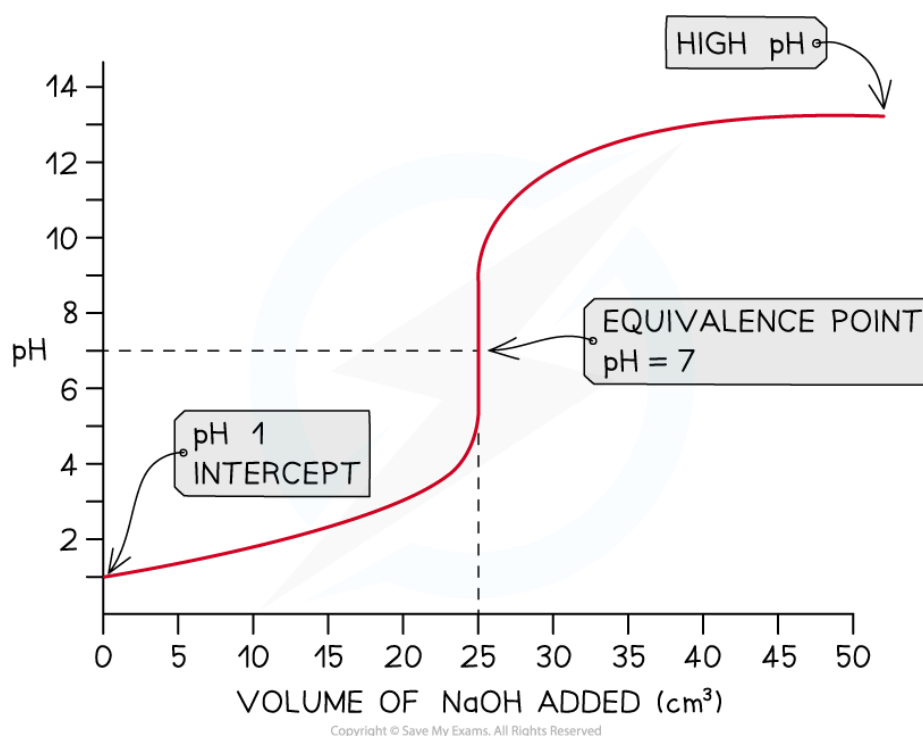
- There are four combinations of acids and alkalis that you should know about:
  - strong acid + strong base
  - weak acid + strong base
  - weak base + strong acid
  - weak acid + weak base

### **Strong Acid + Strong Base**

- In this example, sodium hydroxide, NaOH(aq), is being added to hydrochloric acid, HCl(aq)



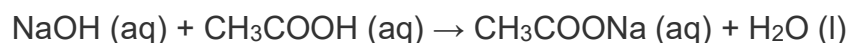
- The pH intercept on the y axis starts at a low pH, roughly 1, due to the relative strength of the hydrochloric acid
- As the NaOH (aq) is added, there is a gradual rise in pH until the titration approaches the equivalence point
- In this case, the pH at equivalence is 7
  - The equivalence point is in the middle of the vertical section of the pH curve
- Once all of the acid has been neutralised, the curve flattens out and continues to rise gradually
- At the end of the titration, the pH will be high due to the relative strength of the sodium hydroxide



*Strong acid - strong base pH curve*

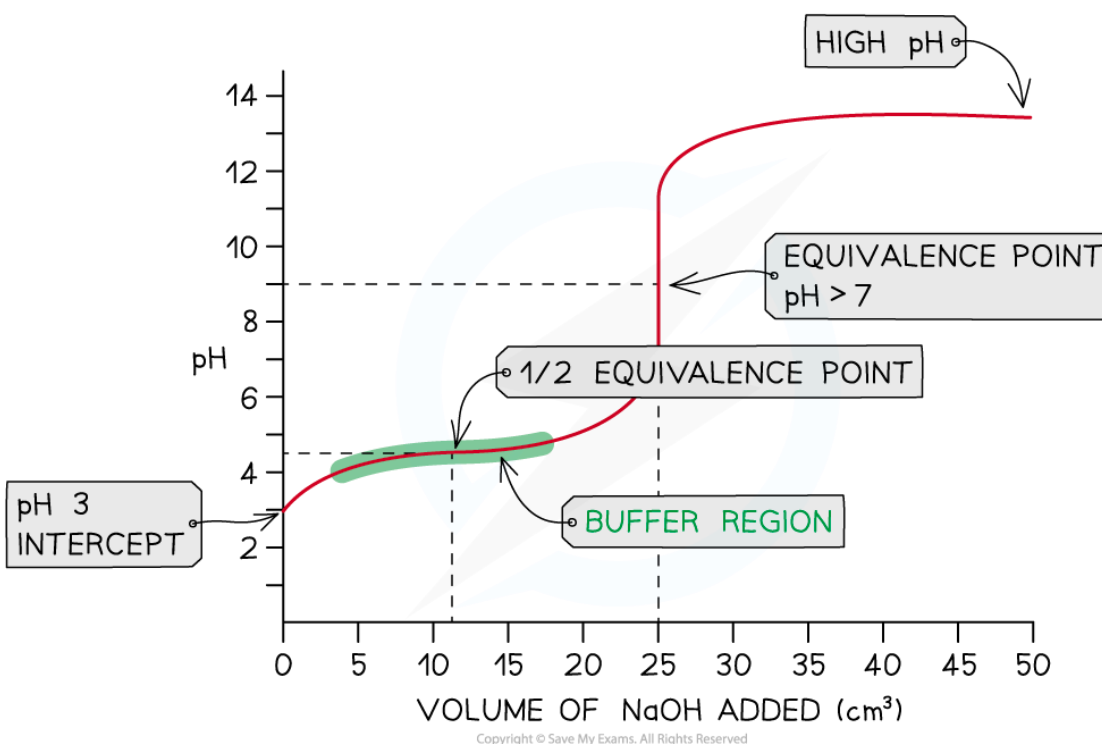
### Weak Acid + Strong Base

- In this example, strong sodium hydroxide, NaOH (aq), is being added to weak ethanoic acid, CH<sub>3</sub>COOH (aq)



- The pH on the intercept on the y axis starts at roughly 3 due to the relative strength of the ethanoic acid
- The initial rise in pH is steep as the neutralisation of the weak acid by the strong base is rapid
- Ethanoate ions (conjugate base to ethanoic acid) are formed which then creates a buffer

- A buffer consists of a weak acid and its conjugate base or a weak base and its conjugate acid
- At this point, the buffer formed will resist changes in pH so the pH rises gradually as shown in the buffer region
- The half equivalence point is the stage of the titration at which exactly half the amount of weak acid has been neutralised
  - $[\text{CH}_3\text{COOH}(\text{aq})] = [\text{CH}_3\text{COO}^-(\text{aq})]$
  - At this point, it is important to note that the  $\text{p}K_a$  of the acid is equal to the pH
    - $\text{p}K_a = \text{pH}$  at half equivalence
- The equivalence point in a weak acid - strong base titration is above 7



*Weak acid - strong base pH curve*

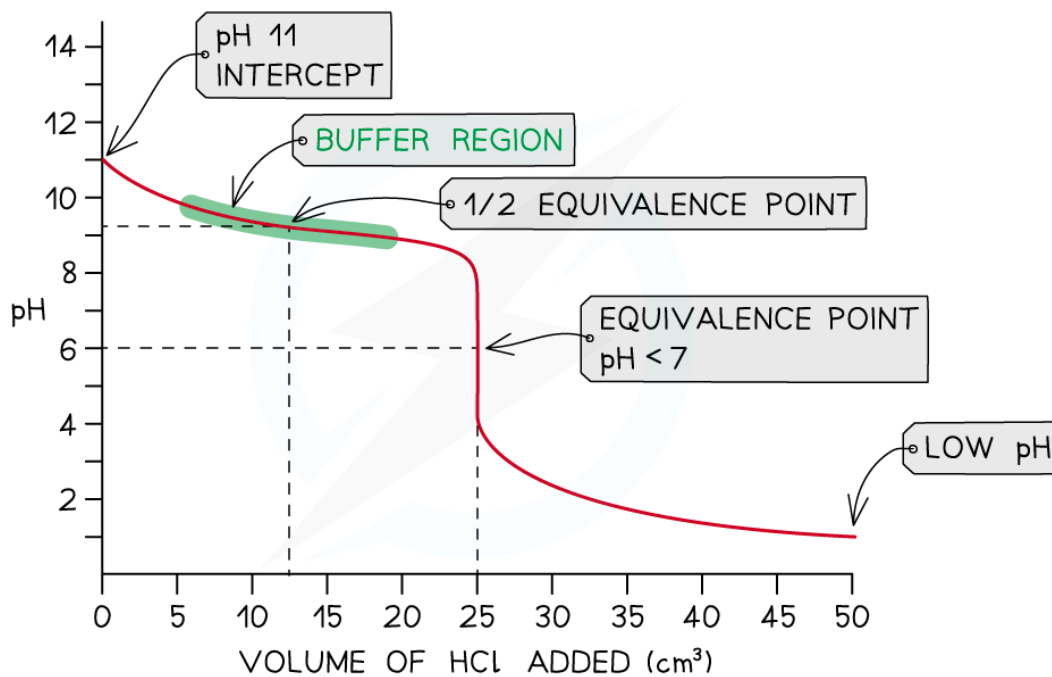
### Weak Base + Strong Acid

- In this example, strong hydrochloric acid,  $\text{HCl}(\text{aq})$ , is being added to weak ammonia,  $\text{NH}_3(\text{aq})$



- The pH on the intercept on the y axis starts at roughly 11 due to the relative strength of the ammonia
- The pH will fall as the ammonia begins to be neutralised and the conjugate acid,  $\text{NH}_4^+(\text{aq})$ , is produced
- This again creates a buffer region so the pH will only fall gradually

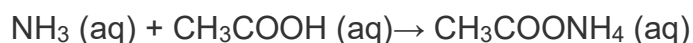
- The half equivalence point is the stage of the titration at which exactly half the amount of weak base has been neutralised
  - $[\text{NH}_3(\text{aq})] = [\text{NH}_4^+(\text{aq})]$
  - At this point it is important to note that the  $\text{p}K_b$  of the base is equal to the  $\text{pOH}$ 
    - $\text{p}K_b = \text{pOH}$  at half equivalence
- The pH at equivalence for a weak base-strong acid is below 7



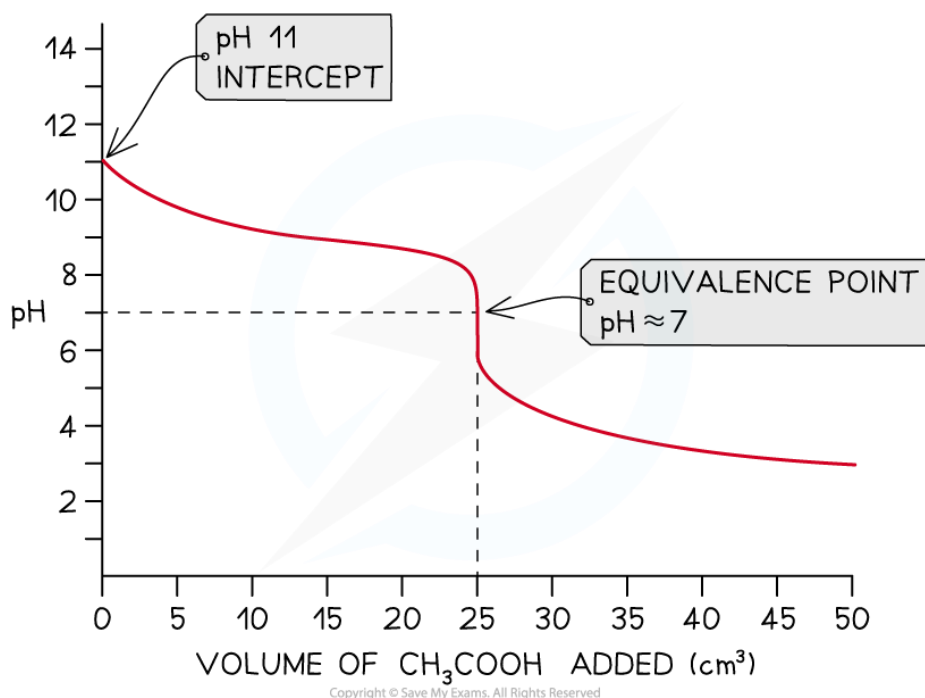
*Weak base - strong acid pH curve*

### Weak Acid + Weak Base

- In this example, weak ethanoic acid,  $\text{CH}_3\text{COOH}(\text{aq})$ , is being added to weak ammonia,  $\text{NH}_3(\text{aq})$



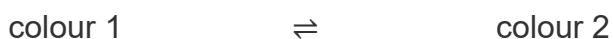
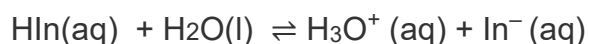
- The starting pH of roughly 11 for the weak base will fall as it begins to neutralise
- The change in pH for this titration is very gradual
  - Note that the vertical section of this pH curve is not steep as with other three so the equivalence point is difficult to determine
  - Therefore this titration is not performed
- The pH at equivalence for a weak acid-weak base is roughly 7 but is difficult to determine



*Weak acid - weak base pH curve*

## Indicators

- An acid-base indicator is a weak acid which dissociates to give an anion of a different colour
- Consider a weak acid, HIn:



- HIn and its conjugate base In<sup>-</sup> are different colours
- The colour of the solution depends on the relative concentrations of the two species
- If the solution is acidic, the above equilibrium will be shifted to the left and more HIn will be present
  - Colour 1 will dominate
- If the solution is alkaline, the above equilibrium will shift to the right and more In<sup>-</sup> will be present
  - Colour 2 will dominate
- The colour of the indicator depends on the pH of the solution
  - The colour does not change suddenly at a certain pH, but changes gradually over a pH range
  - The colour of the indicator depends on the ratio of [HIn] to [In<sup>-</sup>]

- The pH at which these transitions will occur depends on the  $K_a$  of the indicator

$$K_a = \frac{[H^+][In^-]}{[HIn]}$$

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- The endpoint of the reaction is where there is a balance between  $[HIn]$  and  $[In^-]$ . At this point these two concentrations are equal:

$$K_a = \frac{[H^+][In^-]}{[HIn]} = [H^+]$$

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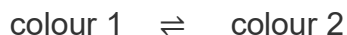
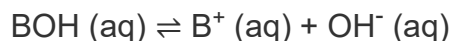
- Taking negative logs of both sides:

$$pK_a = pH$$

- This means the  $pK_a$  of an indicator is the same as the pH of its endpoint
- The colour change for most indicators takes place over a range of  $pH = pK_a \pm 1$

### Weak bases as indicators

- An indicator can also be a weak base:



- For such indicators:
  - Colour 1 is observed in alkaline conditions
  - Colour 2 is observed in acidic conditions

### Choosing a suitable indicator

- Around the equivalence point of a titration, the pH changes very rapidly
- Indicators change colour over a narrow pH range, approximately centred around the  $pK_a$  of the indicator
- An indicator will be appropriate for a titration if the pH range of the indicator falls within the rapid pH change for that titration

## Common Indicators and their colours table

Indicator	Colour in acid	Colour in alkali	pK <sub>a</sub>	pH range of colour change
Thymol blue	red	yellow	1.7	1.2 – 2.8
Methyl orange	red	yellow	3.7	3.1 – 4.4
Bromophenol blue	yellow	blue	4.1	3.4 – 4.6
Methyl red	red	yellow	5.1	4.4 – 6.2
Phenolphthalein	colourless	pink	9.3	8.3 – 10.0

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## Strong acid - strong base

- In strong acid – strong base titrations, the pH changes from 4 to 10 at the end-point so a suitable indicator must change colour within this range
  - Methyl red and phenolphthalein are suitable indicators for these titrations
  - Methyl orange is not ideal but it shows a significant enough colour change at the end point so is widely used

## Weak acid - strong base

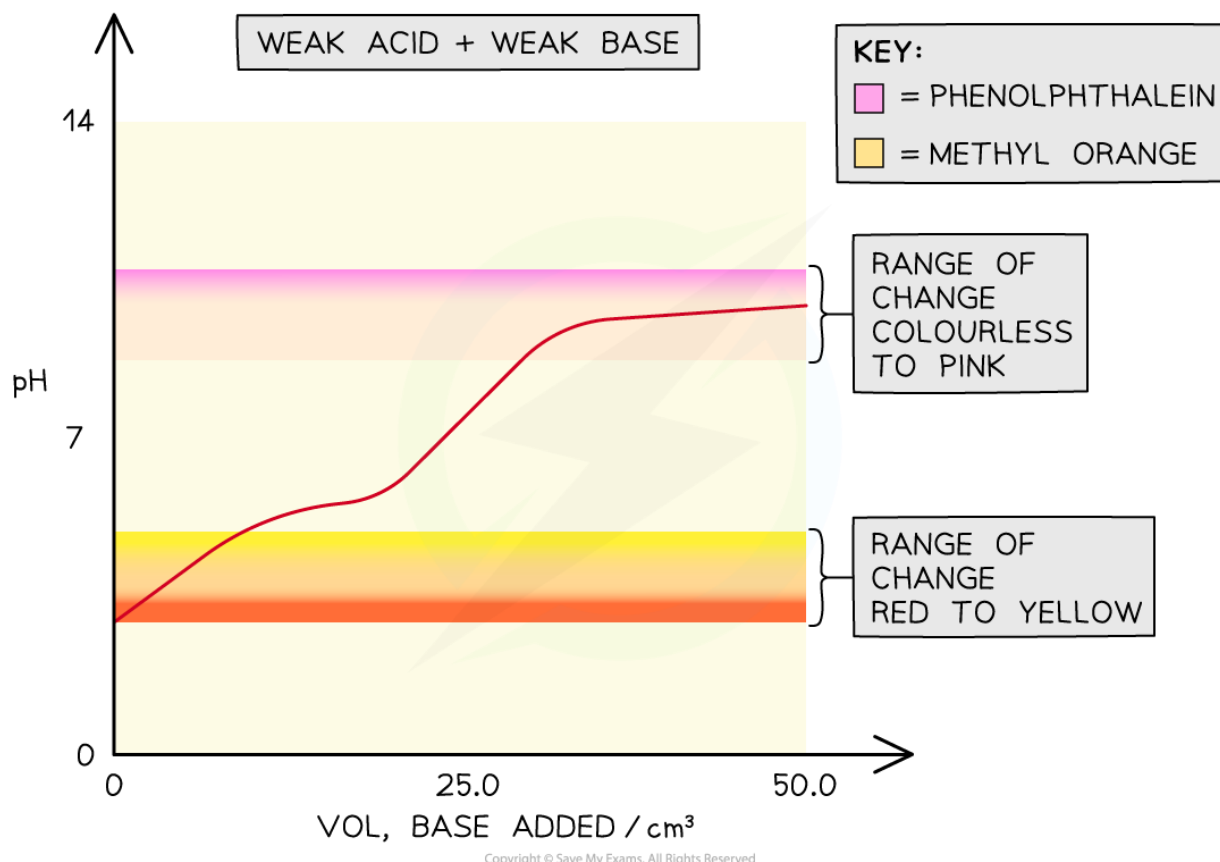
- In weak acid – strong base titrations, the pH changes from 7 to 10 at the end-point so a suitable indicator must change colour within this range
  - Phenolphthalein is the only suitable indicator for weak acid – strong base titrations that is widely available

## Strong acid - weak base

- In strong acid – weak base titrations, the pH changes from 4 to 7 at the end-point so a suitable indicator must change colour within this range
  - Methyl red is the most suitable indicator for these titrations
  - However, methyl orange is often used since it shows a significant enough colour change at the end-point and is more widely available than methyl red

## Weak acid - weak base

- In weak acid - weak alkali titrations, there is no sudden pH change at the end-point and thus there are no suitable indicators for these titrations
  - The end-points of these titrations cannot be easily determined



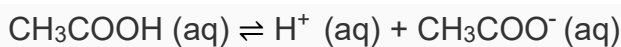
*The overlay on the graph shows that both phenolphthalein and methyl orange would change colour outside the point of inflection in a weak acid-weak base titration so they would not be able to show the equivalence point of the titration*

## Buffers

- A buffer solution is a solution which resists changes in pH when small amounts of acid or base are added
  - A buffer solution is used to keep the pH almost constant
  - A buffer can consist of weak acid – conjugate base or weak base – conjugate acid

### Ethanoic acid & sodium ethanoate as a buffer

- A common buffer solution is an aqueous mixture of ethanoic acid and sodium ethanoate
- Ethanoic acid is a weak acid and partially ionises in solution to form a relatively low concentration of ethanoate ions



ethanoic acid       $\rightleftharpoons$       ethanoate

high conc           $\rightleftharpoons$           low conc

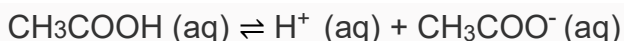
- Sodium ethanoate is a salt which fully ionises in solution



sodium ethanoate → ethanoate ion

low conc. → high conc.

- There are reserve supplies of the acid ( $\text{CH}_3\text{COOH}$ ) and its conjugate base ( $\text{CH}_3\text{COO}^-$ )
  - The buffer solution contains relatively high concentrations of  $\text{CH}_3\text{COOH}$  (due to the partial ionisation of ethanoic acid) and  $\text{CH}_3\text{COO}^-$  (due to the full ionisation of sodium ethanoate)
- In the buffer solution, the ethanoic acid is in equilibrium with hydrogen and ethanoate ions



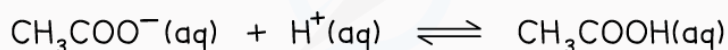
high conc.

high conc.

Adding  $\text{H}^+$  ions to a buffer solution:

- The equilibrium position shifts to the left as  $\text{H}^+$  ions react with  $\text{CH}_3\text{COO}^-$  ions to form more  $\text{CH}_3\text{COOH}$  until equilibrium is re-established
- As there is a large reserve supply of  $\text{CH}_3\text{COO}^-$ , the concentration of  $\text{CH}_3\text{COO}^-$  in solution doesn't change much as it reacts with the added  $\text{H}^+$  ions
- As there is a large reserve supply of  $\text{CH}_3\text{COOH}$ , the concentration of  $\text{CH}_3\text{COOH}$  in solution doesn't change much as  $\text{CH}_3\text{COOH}$  is formed from the reaction of  $\text{CH}_3\text{COO}^-$  with  $\text{H}^+$
- As a result, the pH remains reasonably constant

ETHANOATE IONS IN THE BUFFER SOLUTION REACT WITH THE ADDED  $\text{H}^+$  IONS TO PREVENT THE pH FROM DECREASING

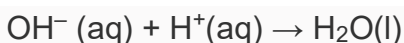


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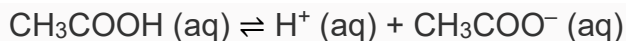
*When hydrogen ions are added to the solution the pH of the solution would decrease. However, the ethanoate ions in the buffer solution react with the hydrogen ions to prevent this and keep the pH constant*

Adding  $\text{OH}^-$  ions to a buffer solution:

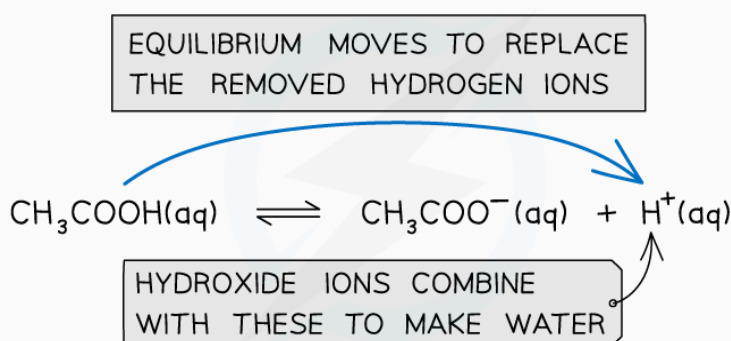
- The  $\text{OH}^-$  reacts with  $\text{H}^+$  to form water



- The  $\text{H}^+$  concentration decreases
- The equilibrium position shifts to the right and more  $\text{CH}_3\text{COOH}$  molecules ionise to form more  $\text{H}^+$  and  $\text{CH}_3\text{COO}^-$  until equilibrium is re-established



- As there is a large reserve supply of  $\text{CH}_3\text{COOH}$ , the concentration of  $\text{CH}_3\text{COOH}$  in solution doesn't change much when  $\text{CH}_3\text{COOH}$  dissociates to form more  $\text{H}^+$  ions
- As there is a large reserve supply of  $\text{CH}_3\text{COO}^-$ , the concentration of  $\text{CH}_3\text{COO}^-$  in solution doesn't change much
- As a result, the pH remains reasonably constant



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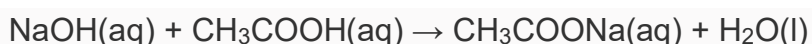
*When hydroxide ions are added to the solution, the hydrogen ions react with them to form water; The decrease in hydrogen ions would mean that the pH would increase however the equilibrium moves to the right to replace the removed hydrogen ions and keep the pH constant*

### Exam Tip

Remember that buffer solutions cannot cope with excessive addition of acids or alkalis as their pH will change significantly. The pH will only remain relatively constant if small amounts of acids or alkalis are added.

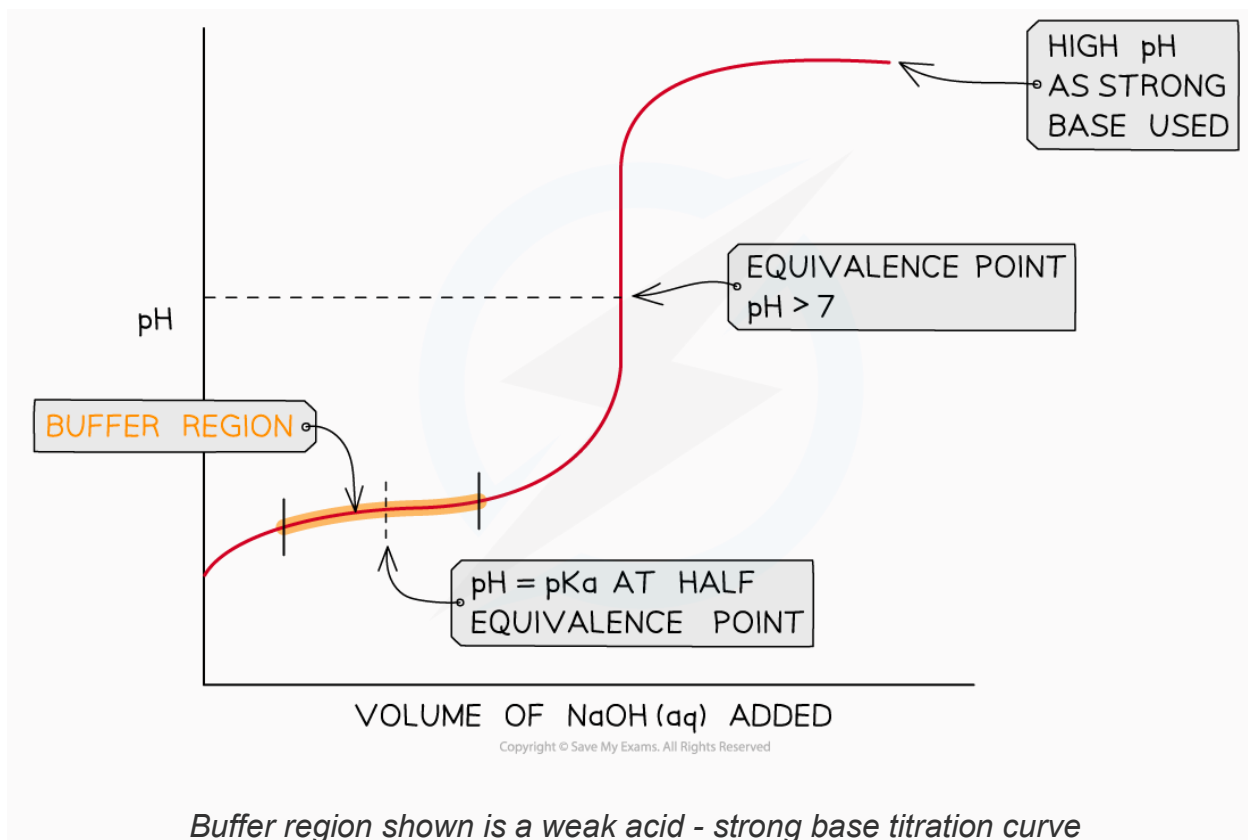
### The Buffer Region

- These are seen on a pH curve and represent the region where small additions in acid or base result in little change in the overall pH of the solution
- For a weak acid - strong base titration between sodium hydroxide,  $\text{NaOH}(\text{aq})$ , and ethanoic acid,  $\text{CH}_3\text{COOH}(\text{aq})$



- The initial rise in pH is steep as the neutralisation of the weak acid by the strong base is rapid
- Sodium ethanoate is then formed which creates a buffer that will resist changes in pH so the pH rises gradually
  - A buffer consists of a weak acid and its conjugate salt

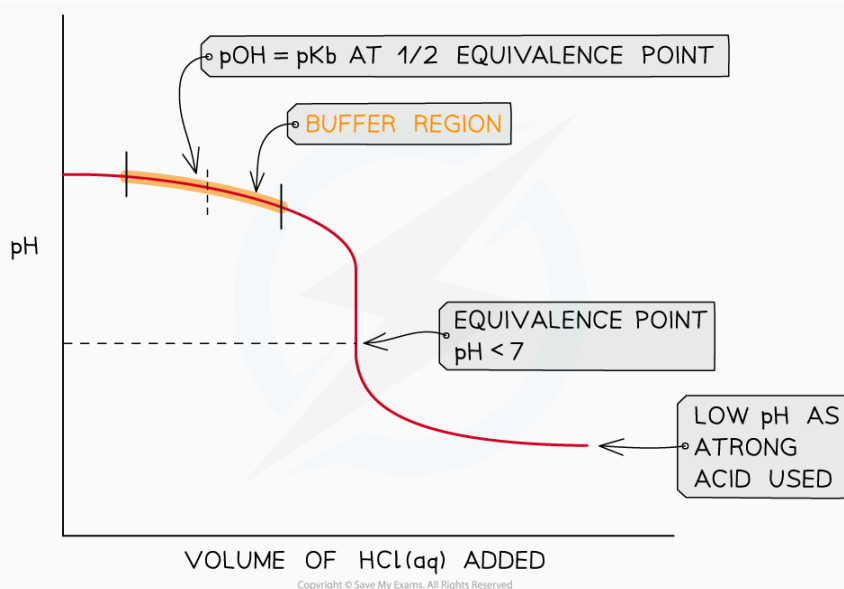
- This section of the curve is known as the buffer region
- Only small increases in pH are seen when the strong base is added in this part of the titration curve
- At this point, the acid is in equilibrium with the salt ion
  - $\text{CH}_3\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+(\text{aq})$
- Continuing to add the strong base will 'use up' all of the acid so the forward reaction will then be favoured



- A buffer region is also observed during a weak base - strong acid titration
  - Ammonia,  $\text{NH}_3(\text{aq})$ , and hydrochloric acid,  $\text{HCl}(\text{aq})$ , is a common example



- The starting pH of the weak base will fall as it begins to be neutralised and the conjugate acid,  $\text{NH}_4^+(\text{aq})$ , will be produced
- This results in a buffer that resists change in pH
- Due to this, the pH will only fall gradually



*Buffer region shown is a weak base - strong acid titration curve*

## Salt Hydrolysis

- An ionic salt is formed from the neutralisation reaction of an acid and base

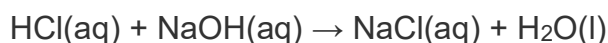


### *Neutralisation*

- The ionic salt, MA, formed will dissociate in water
  - Hydrolysis is where water is used to break a bond within a compound, which results in the aqueous ions for an ionic salt
- The reaction of the salt will vary depending on the strength of the acids and bases used in the neutralisation reaction
- The use of the differing strengths of the acids and bases will directly influence the type of salt hydrolysis and the pH of the final solution

### Strong Acids and Strong Bases

- A common example of this is the reaction between hydrochloric acid, HCl (aq), and sodium hydroxide (aq):



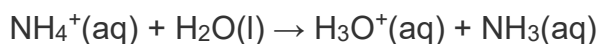
- The Na<sup>+</sup> and Cl<sup>-</sup> ions do not act as Brønsted-Lowry acids or bases as they can not release or accept H<sup>+</sup> ions
- Therefore, they do not affect the pH

### Strong Acid and Weak Base

- The salt formed by a strong acid such as hydrochloric acid,  $\text{HCl}(\text{aq})$ , and a weak base such as ammonia,  $\text{NH}_3(\text{aq})$ , will form an acidic solution:



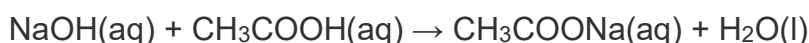
- In this reaction, the conjugate acid of ammonia is formed,  $\text{NH}_4^+$ , and can react with water to produce  $\text{H}_3\text{O}^+$



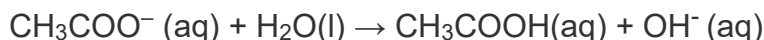
- Therefore, the solution becomes more acidic
- The hydrolysis of this salt demonstrates why the equivalence point of a strong acid - weak base pH curve is below 7

### Strong Base and Weak Acid

- The salt formed by a strong base such as sodium hydroxide,  $\text{NaOH}(\text{aq})$ , and a weak acid such as ethanoic acid,  $\text{CH}_3\text{COOH}(\text{aq})$ , will form an alkaline solution:



- In this reaction, the conjugate base of ethanoic acid is produced,  $\text{CH}_3\text{COO}^-(\text{aq})$ , and this will react with water to form hydroxide ions,  $\text{OH}^-(\text{aq})$



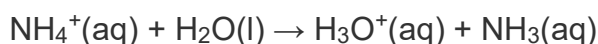
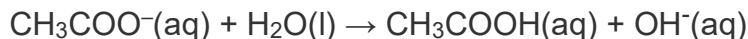
- Therefore, the solution becomes more basic
- The hydrolysis of this salt demonstrates why the equivalence point of a strong base - weak acid pH curve is above 7

### Weak Acid and Weak Base

- In order to determine the pH of the resulting solution of a reaction between a weak acid and weak base we must take into account the  $K_a$  and  $K_b$  values
- Using the reaction between ammonia,  $\text{NH}_3(\text{aq})$ , and ethanoic acid,  $\text{CH}_3\text{COOH}(\text{aq})$ , as an example:



- Both the cation (positive ion) and anion ion (negative) produced will have acid-base properties



$$K_a (\text{CATION}) = \frac{K_w}{K_b (\text{PARENT BASE})}$$

$$K_b (\text{ANION}) = \frac{K_w}{K_a (\text{PARENT ACID})}$$

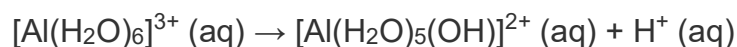
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*How to calculate the vales for the values of  $K_a$  (cation) and  $K_b$  (anion)*

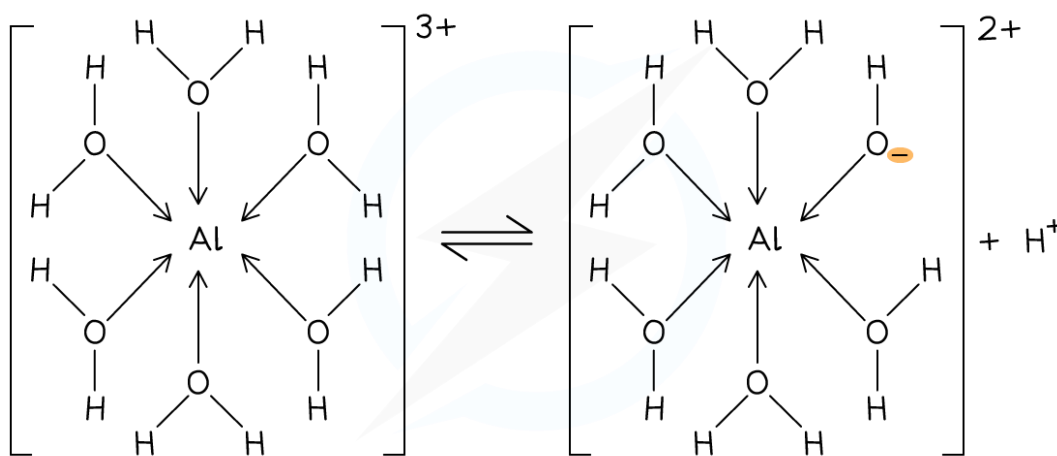
- If the  $K_a$  is larger, the solution will be acidic
- If the  $K_b$  is larger the solution will be basic
- If  $K_a = K_b$ , then the pH will be 7

### Metals

- Small metal ions that have a high charge will exhibit a high charge density
  - An example is  $\text{Al}^{3+}$
- This makes the highly charged metal ions ideal for forming complexes as they can coordinately bond with ligands
- The complex formed can then act as a weak acid by releasing hydrogen ions when hydrolysed,  $\text{H}^+$
- The high charge density of the metal ion increases the polarity of the water molecule pulling the electrons towards itself, until the O-H bond finally breaks



- The metal ion must have a high enough charge and small radius for this to occur, consequently, 1+ and 2+ ions will not release  $\text{H}^+$  ions and therefore decrease the pH of a solution



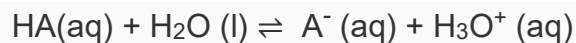
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*The  $[\text{Al}(\text{H}_2\text{O})_6]^{3+} (\text{aq})$  releases an  $\text{H}^+$  ion decreasing the pH of the solution*

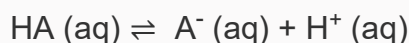
## Acid & Base Dissociation Constants

## Weak acids

- A weak acid is an acid that partially (or incompletely) dissociates in aqueous solutions
  - For example, most carboxylic acids (e.g. ethanoic acid), HCN (hydrocyanic acid), H<sub>2</sub>S (hydrogen sulfide) and H<sub>2</sub>CO<sub>3</sub> (carbonic acid)
  - In general, the following equilibrium is established:



OR



- At equilibrium, the majority of HA molecules remain unreacted
- The position of the equilibrium is more over to the left and an equilibrium is established
- As this is an equilibrium, we can write an equilibrium constant expression for the reaction
- This constant is called the acid dissociation constant, K<sub>a</sub>, and has the units mol dm<sup>-3</sup>

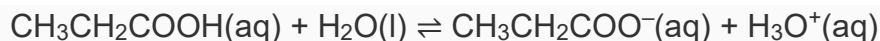
$$K_a = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]}$$

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

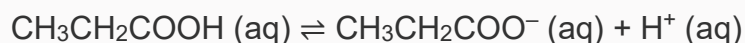
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*Acid dissociation constant expressions*

- Carboxylic acids are weak acids
  - For example, propanoic acid, CH<sub>3</sub>CH<sub>2</sub>COOH (aq), dissociates according to the following equation which leads to the K<sub>a</sub> expression for propanoic acid:



OR



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

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

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*Acid dissociation constant expressions for propanoic acid*

- Values of  $K_a$  are very small
  - For example,  $K_a$  for propanoic acid =  $1.34 \times 10^{-5} \text{ mol dm}^{-3}$
- When writing the equilibrium expression for weak acids, we assume that the concentration of  $\text{H}_3\text{O}^+$  (aq) due to the ionisation of water is negligible

### Weak bases

- A weak base will also ionise in water and we can represent this with the base dissociation constant,  $K_b$
- In general the equilibrium established is:

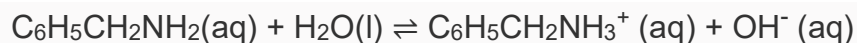


$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

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*Base dissociation constant expression*

- Amines are weak bases
  - For example, 1-phenylmethanamine,  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2(\text{aq})$ , dissociates according to the following equation which leads to the  $K_a$  expression for 1-phenylmethanamine:



$$K_b = \frac{[\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2]}$$

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*Base dissociation constant expression for 1-phenylmethanamine*

### pKa and pKb

- The range of values of  $K_a$  and  $K_b$  is very wide and for weak acids, the values themselves are very small numbers

Table of  $K_a$  values

Acid	$K_a / \text{mol dm}^{-3}$
Methanoic, $\text{HCOOH}$	$1.77 \times 10^{-4}$
Ethanoic, $\text{CH}_3\text{COOH}$	$1.74 \times 10^{-5}$
Benzoic, $\text{C}_6\text{H}_5\text{COOH}$	$6.46 \times 10^{-5}$
Carbonic, $\text{H}_2\text{CO}_3$	$4.30 \times 10^{-7}$

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- For this reason, it is easier to work with another term called **pKa** for acids or pKb for bases
- In order to convert the values we need to apply the following calculations:

$$\text{p}K_a = -\log K_a \quad K_a = 10^{-\text{p}K_a}$$

$$\text{p}K_b = -\log K_b \quad K_b = 10^{-\text{p}K_b}$$

Table of pKa values

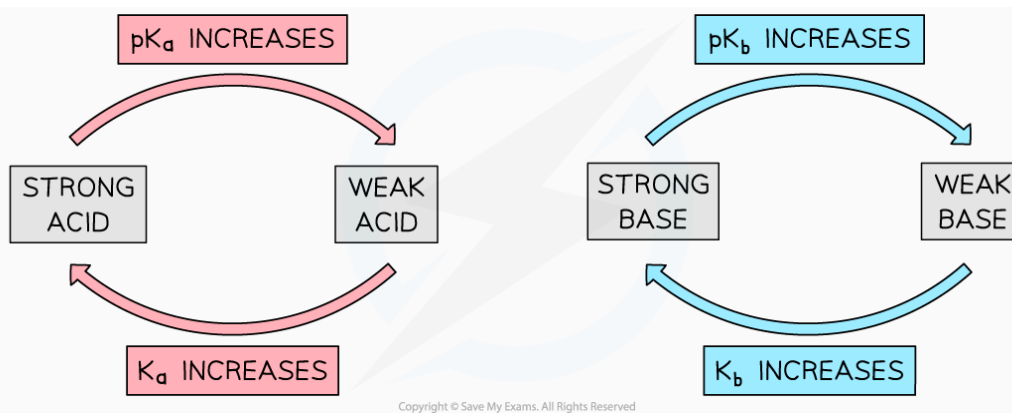
Acid	$K_a / \text{mol dm}^{-3}$	pKa
Methanoic, $\text{HCOOH}$	$1.77 \times 10^{-4}$	3.75
Ethanoic, $\text{CH}_3\text{COOH}$	$1.74 \times 10^{-5}$	4.75
Benzoic, $\text{C}_6\text{H}_5\text{COOH}$	$6.46 \times 10^{-5}$	4.18
Carbonic, $\text{H}_2\text{CO}_3$	$4.30 \times 10^{-7}$	6.36

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- The range of pKa values for most weak acids lies between 3 and 7

### Relative Strengths of Acids and Bases

- The larger the  $K_a$  value, the stronger the acid
- The larger the pKa value, the weaker the acid
- The larger the  $K_b$  value, the stronger the base
- The larger the pKb value, the weaker the base

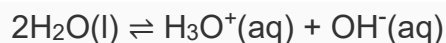


$pK_a$  and  $pK_b$  tell us the relative strengths of acids and bases

## Relating $K_w$ to $K_a$

### The Ionic Product of Water and Temperature

- In all aqueous solutions, an equilibrium exists in water where a few water molecules dissociate into protons and hydroxide ions
- We can derive an equilibrium constant for the reaction:



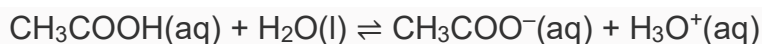
- The concentration of water is constant, so the expression for  $K_w$  is:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

- This is a specific equilibrium constant called the ionic product for water
- The product of the two ion concentrations is  $1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$  at  $25^\circ\text{C}$
- For conjugate acid-base pairs,  $K_a$  and  $K_b$  are related to  $K_w$

$$K_a \times K_b = K_w$$

- The conjugate base of ethanoic acid is the ethanoate ion,  $\text{CH}_3\text{COO}^- (\text{aq})$



acid

conjugate base

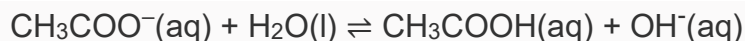
- We can then put this in to the  $K_a$  expression

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

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*Acid dissociation constant for ethanoic acid*

- The ethanoate ion will react with water according to the following equation



- We can then put this in to the  $K_b$  expression

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

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*Base dissociation constant for the ethanoate ion*

- Now, these two expressions can be combined, which corresponds to
  - $K_a \times K_b = K_w$
  - $K_a \times K_b = 10^{-14}$
- Or we could say that
  - $\text{p}K_a + \text{p}K_b = \text{p}K_w$
  - $\text{p}K_a + \text{p}K_b = 14$
  - This makes the numbers much more easy to deal with as using  $K_a K_b = 10^{-14}$  will give very small numbers

$$K_a K_b = \frac{[\cancel{\text{CH}_3\text{COO}^-}][\text{H}_3\text{O}^+]}{[\cancel{\text{CH}_3\text{COOH}}]} \times \frac{[\cancel{\text{CH}_3\text{COOH}}][\text{OH}^-]}{[\cancel{\text{CH}_3\text{COO}^-}]}$$

$$= [\text{H}_3\text{O}^+][\text{OH}^-] = K_w$$

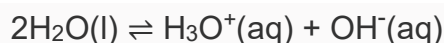
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*Combining  $K_a K_b$  expressions*

- Or rearranging these:
  - $K_a = K_w / K_b$
  - $K_b = K_w / K_a$

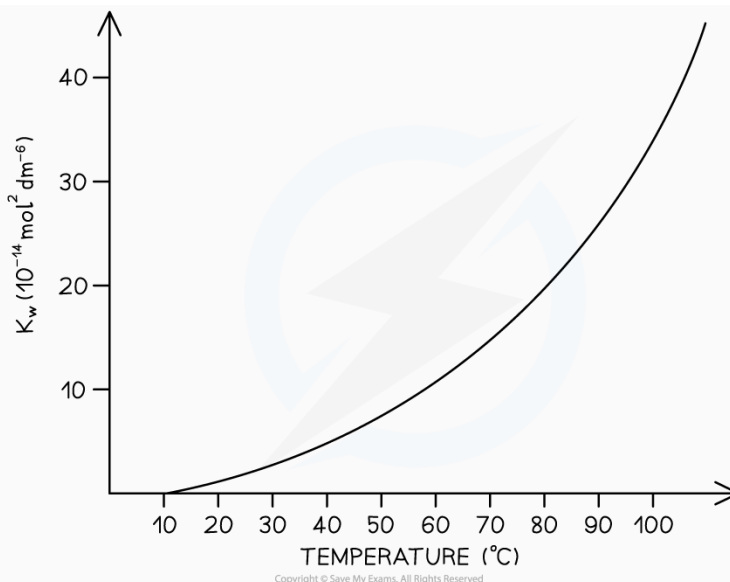
### The ionic product of water, $K_w$

- The ionisation of water is an endothermic process



- In accordance with Le Châtelier's principle, an increase in temperature will result in the forward reaction being favoured
  - This causes an increase in the concentration of the hydrogen and hydroxide ions
  - This leads to the magnitude of  $K_w$  increasing
  - Therefore, the pH will decrease
- Increasing the temperature, decreases the pH of water (becomes more acidic)

- Decreasing the temperature, increases the pH of water (becomes more basic)



*Relationship between  $K_w$  and temperature*

## Acid & Base Calculations

### pH

- The acidity of an aqueous solution depends on the number of  $\text{H}_3\text{O}^+$  ions in solution
- pH is defined as:

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

- Where  $[\text{H}_3\text{O}^+]$  is the concentration of  $\text{H}_3\text{O}^+$  ions in  $\text{mol dm}^{-3}$

Similarly, the concentration of  $\text{H}^+$  of a solution can be calculated if the pH is known by rearranging the above equation to:

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

- The pH scale is a logarithmic scale with base 10
- This means that each value is 10 times the value below it
  - For example, pH 5 is 10 times more acidic than pH 6
- pH values are usually given to 2 decimal places

### pOH

- The basicity of an aqueous solution depends on the number of hydroxide ions,  $\text{OH}^-$ , in solution
- pOH is defined as:

$$\text{pOH} = -\log [\text{OH}^-]$$

- Where  $[\text{OH}^-]$  is the concentration of hydroxide ions in  $\text{mol dm}^{-3}$

Similarly, the concentration of  $\text{OH}^-$  of a solution can be calculated if the pH is known by rearranging the above equation to:

$$[\text{OH}^-] = 10^{-\text{pOH}}$$

- If you are given the concentration of a basic solution and need to find the pH, this can be done by:

$$[\text{H}_3\text{O}^+] = K_w / [\text{OH}^-]$$

- Alternatively, if you are given the  $[\text{OH}^-]$  and calculate the pOH, the pH can be found by:

$$\text{pH} = 14 - \text{pOH}$$

### Worked example

pH and  $\text{H}_3\text{O}^+$  calculations

1. Find the pH when the hydrogen ion concentration is  $1.60 \times 10^{-4} \text{ mol dm}^{-3}$
2. Find the hydrogen ion concentration when the pH is 3.10

Answers

Answer 1:

The pH of the solution is:

- $\text{pH} = -\log [\text{H}_3\text{O}^+]$ 
  - $\text{pH} = -\log 1.6 \times 10^{-4}$
  - $\text{pH} = 3.80$

Answer 2:

The hydrogen concentration can be calculated by rearranging the equation for pH

- $\text{pH} = -\log [\text{H}_3\text{O}^+]$
- $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$ 
  - $[\text{H}_3\text{O}^+] = 10^{-3.10}$
  - $[\text{H}_3\text{O}^+] = 7.94 \times 10^{-4} \text{ mol dm}^{-3}$

### Worked example

pH calculations of a strong alkali

1. Calculate the pH of  $0.15 \text{ mol dm}^{-3}$  sodium hydroxide, NaOH
2. Calculate the hydroxide concentration of a solution of sodium hydroxide when the pH is 10.50

## Answers

Sodium hydroxide is a strong base which ionises as follows:



Answer 1:

The pH of the solution is:

- $[\text{H}^+] = K_w \div [\text{OH}^-]$ 
  - $[\text{H}^+] = (1 \times 10^{-14}) \div 0.15 = 6.66 \times 10^{-14}$
- $\text{pH} = -\log[\text{H}^+]$ 
  - $\text{pH} = -\log 6.66 \times 10^{-14} = 13.17$

Answer 2

Step 1: Calculate hydrogen concentration by rearranging the equation for pH

- $\text{pH} = -\log[\text{H}^+]$
- $[\text{H}^+] = 10^{-\text{pH}}$ 
  - $[\text{H}^+] = 10^{-10.50}$
  - $[\text{H}^+] = 3.16 \times 10^{-11} \text{ mol dm}^{-3}$

Step 2: Rearrange the ionic product of water to find the concentration of hydroxide ions

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

Step 3: Substitute the values into the expression to find the concentration of hydroxide ions

- Since  $K_w$  is  $1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ 
  - $[\text{OH}^-] = (1 \times 10^{-14}) \div (3.16 \times 10^{-11})$
  - $[\text{OH}^-] = 3.16 \times 10^{-4} \text{ mol dm}^{-3}$

## K<sub>a</sub>, pK<sub>a</sub>, K<sub>b</sub> and pK<sub>b</sub>

- In reactions of weak acids and bases, we cannot make the same assumptions as for the ionisation of strong acids and bases
- For a weak acid and its conjugate base, we can use the equation:

$$K_w = K_a \times K_b$$

- By finding the -log of these, we can use:

$$pK_w = pK_a + pK_b$$

- Remember, to convert these terms you need to use:

$$pK_a = -\log K_a \quad K_a = 10^{-pK_a}$$

$$pK_b = -\log K_b \quad K_b = 10^{-pK_b}$$

- The assumptions we must make when calculating values for  $K_a$ ,  $pK_a$ ,  $K_b$  and  $pK_b$  are:
  - The initial concentration of acid  $\approx$  the equilibrium concentration of acid
  - $[A^-] = [H_3O^+]$
  - There is negligible ionisation of the water, so  $[H_3O^+]$  is not affected
  - The temperature is 25 °C

### Worked example

Calculate the acid dissociation constant,  $K_a$ , at 298 K for a 0.20 mol dm<sup>-3</sup> solution of propanoic acid with a pH of 4.88.

Answer

Step 1: Calculate  $[H_3O^+]$  using

- $[H_3O^+] = 10^{-pH}$ 
  - $[H_3O^+] = 10^{-4.88}$
  - $[H_3O^+] = 1.3182 \times 10^{-5}$

Step 2: Substitute values into  $K_a$  expression

- $K_a = [H_3O^+]^2 / [CH_3CH_2COOH]$ 
  - $K_a = (1.3182 \times 10^{-5})^2 / 0.2$
  - $K_a = 8.70 \times 10^{-10} \text{ mol dm}^{-3}$

### Worked example

A 0.035 mol dm<sup>-3</sup> sample of methylamine ( $CH_3NH_2$ ) has  $pK_b$  value of 3.35 at 298 K. Calculate the pH of methylamine.

Answer

Step 1: Calculate the value for  $K_b$  using

- $K_b = 10^{-pK_b}$ 
  - $K_b = 10^{-3.35}$
  - $K_b = 4.4668 \times 10^{-4}$

Step 2: Substitute values into  $K_b$  expression to calculate  $[\text{OH}^-]$

- $K_b = [\text{OH}^-]^2 / [\text{CH}_3\text{NH}_2]$
- $4.4668 \times 10^{-4} = [\text{OH}^-]^2 / 0.035$
- $[\text{OH}^-] = \sqrt{(4.4668 \times 10^{-4} \times 0.035)}$
- $[\text{OH}^-] = 3.9539 \times 10^{-3}$

Step 3: Calculate the pH

- $[\text{H}^+] = K_w \div [\text{OH}^-]$ 
  - $[\text{H}^+] = (1 \times 10^{-14}) \div 3.9539 \times 10^{-3}$
  - $[\text{H}^+] = 2.5290 \times 10^{-12}$
- $\text{pH} = -\log [\text{H}^+]$ 
  - $\text{pH} = 2.5290 \times 10^{-12}$
  - $\text{pH} = 11.60$  to 2 decimal places

OR

Step 3: Calculate pOH and therefore pH

- $\text{pOH} = -\log [\text{OH}^-]$ 
  - $\text{pOH} = -\log 3.9539 \times 10^{-3}$
  - $\text{pOH} = 2.4029$
- $\text{pH} = 14 - \text{pOH}$ 
  - $\text{pH} = 14 - 2.4029$
  - $\text{pH} = 11.60$  to 2 decimal places