Edexcel International A Level (IAL) Chemistry

Your notes

Acid-base Equilibria

Contents

Your notes

Brønsted–Lowry Acids & Bases

- **The Brønsted–Lowry Theory** defines acids and bases in terms of proton transfer between chemical compounds
- A **Brønsted acid** is a species that can donate a proton
  - For example, hydrogen chloride (HCl) is a Brønsted acid as it can lose a proton to form a hydrogen (H^+) and chloride (Cl^-) ion

$$\mathbf{HCl\,(aq) \rightarrow H^+\,(aq) + Cl^-\,(aq)}$$

- A **Brønsted base** is a species that can accept a proton
  - For example, a hydroxide (OH^-) ion is a Brønsted base as it can accept a proton to form water

$$\mathbf{OH^-\,(aq) + H^+\,(aq) \rightarrow H_2O\,(l)}$$

Conjugate acid–base pairs

- **Conjugate acid–base pairs** are a pair of reactants and products that are linked to each other by the transfer of a proton
- In a reaction equilibrium, the products are formed at the same rate as the reactants are used

$$CH_3COOH\,(aq) + H_2O\,(l) \rightleftharpoons CH_3COO^-\,(aq) + H_3O^+\,(aq)$$

acid base conjugate base conjugate acid

- The reactant CH_3COOH is linked to the product CH_3COO^- by the transfer of a **proton** from the acid to the base
- Similarly, the H_2O molecule is linked to H_3O^+ ion by the transfer of a proton
- These pairs are therefore called **conjugate acid–base pairs**
  - **Conjugate** here means related
  - In other words, the acid and base are related to each other by one proton difference

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pH – Introduction

- The acidity of an aqueous solution depends on the number of H^+ ions in solution
- The **pH** is defined as:

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

- where $[H^+]$ is the concentration of hydrogen ions in mol dm^{-3}
- Similarly, the **concentration of H^+** of a solution can be calculated if the pH is known by rearranging the above equation to:

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

- 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
- The relationship between concentration is easily seen on the following table

pH & [H+] Table

$[H^+]$	Scientific notation	pH
1.0	10^0	0
0.1	10^{-1}	1
0.01	10^{-2}	2
0.001	10^{-3}	3
0.0001	10^{-4}	4
–	10^{-x}	x

pH – Calculations

Worked Example

pH and H^+ calculations

Question 1: Find the pH when the hydrogen concentration is 1.60×10^{-4} mol dm^{-3}

Question 2: Find the hydrogen concentration when the pH is 3.10

Answer

Answer 1:

The pH of the solution is:

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

$= -\log 1.6 \times 10^{-4}$

$= 3.80$

Answer 2:

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

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

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

$= 10^{-3.10}$

$= 7.94 \times 10^{-4}$ mol dm^{-3}

Your notes

Worked Example

Powers of 10

10.0 cm^3 of an aqueous solution of an acid of pH = 1.0 is mixed with 990.0 cm^3 of distilled water. What is the pH of the final solution?

A. 1

B. 2

C. 3

D. 10

Answer

The correct option is **C**.

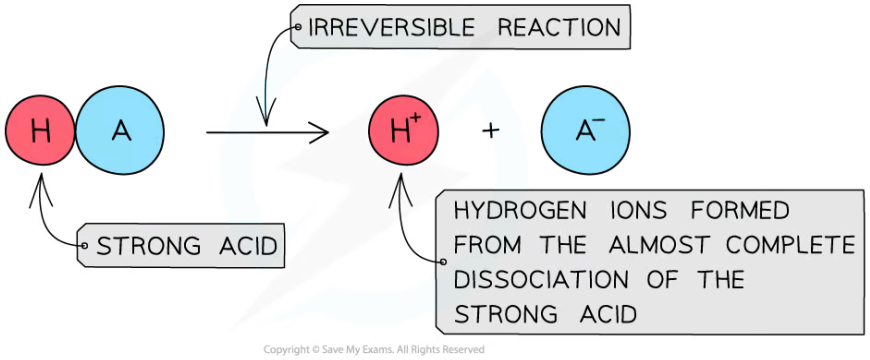
- The total volume after dilution is 1000.0 cm^3 so the concentration of H^+ has been **reduced** by a factor of 100 or 10^{-2}, which means an increase of 2 pH units
    - The final solution is therefore **pH 3**

Your notes

Acids – Dissociation

Strong acids

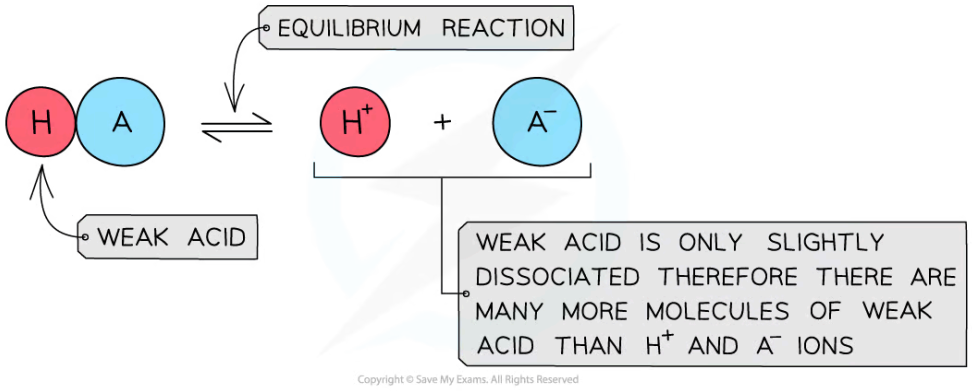
- A **strong acid** is an acid that **dissociates** almost **completely** in aqueous solutions
  - HCl (hydrochloric acid), HNO_3 (nitric acid) and H_2SO_4 (sulfuric acid)
- The position of the equilibrium is so far over to the **right** that you can represent the reaction as an irreversible reaction



The diagram shows the complete dissociation of a strong acid in aqueous solution

Weak acids

- A **weak acid** is an acid that **partially** (or incompletely) **dissociates** in aqueous solutions
  - Eg. most organic acids (ethanoic acid), HCN (hydrocyanic acid), H_2S (hydrogen sulfide) and H_2CO_3 (carbonic acid)
- The position of the equilibrium is more over to the **left** and an equilibrium is established



The diagram shows the partial dissociation of a weak acid in aqueous solution

Acids – Ka Expressions

Your notes

- For weak acids as there is an equilibrium we can write an equilibrium constant expression for the reaction

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

- This constant is called the **acid dissociation constant**, K_a, and has the units mol dm^{-3}
- Values of K_a are very small, for example for ethanoic acid $K_a = 1.74 \times 10^{-5}$ mol dm^{-3}
- When writing the equilibrium expression for weak acids, the following assumptions are made:
  - The concentration of hydrogen ions due to the ionisation of water is negligible
- The value of K_a indicates the extent of dissociation
  - The higher the value of K_a the more dissociated the acid and the stronger it is
  - The lower the value of K_a the weaker the acid

pK_a

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

Table of K_a values

Acid	K_a / mol dm^{-3}
Methanoic, HCOOH	1.77×10^{-4}
Ethanoic, CH_3COOH	1.74×10^{-5}
Benzoic, C_6H_5COOH	6.46×10^{-5}
Carbonic, H_2CO_3	4.30×10^{-7}

- For this reason it is easier to work with another term called pK_a
- The pK_a is the negative log of the K_a value, so the concept is analogous to converting $[H^+]$ into pH values

$$pK_a = -\log K_a$$

- Looking at the pK_a values for the same acids:

Table of pK_a values

Acid	K_a / mol dm^{-3}	pKa
Methanoic, HCOOH	1.77×10^{-4}	3.75
Ethanoic, CH_3COOH	1.74×10^{-5}	4.75
Benzoic, C_6H_5COOH	6.46×10^{-5}	4.18
Carbonic, H_2CO_3	4.30×10^{-7}	6.36

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

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Acids – pH Calculations

Strong acids

- **Strong acids** are completely **ionised** in solution

$$HA\,(aq) \rightarrow H^+\,(aq) + A^-\,(aq)$$

- Therefore, the concentration of hydrogen ions, H^+, is **equal** to the concentration of acid, HA
- The number of hydrogen ions formed from the ionisation of water is **very small** relative to the $[H^+]$ due to ionisation of the strong acid and can therefore be **neglected**
- The **total** $[H^+]$ is therefore the same as the [HA]

Worked Example

What is the pH of 0.01 mol dm^{-3} hydrochloric acid?

Answer

$[HCl] = [H^+] = 0.01\ mol\ dm^{-3}$

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

$pH = -\log[0.01] = 2.00$

The pH of dibasic acids

- Dibasic or diprotic acids have two replaceable protons and will react in a 1:2 ratio with bases
- Sulfuric acid is an example

$$H_2SO_4\,(aq) + 2NaOH\,(aq) \rightarrow Na_2SO_4\,(aq) + 2H_2O\,(l)$$

- You might think that being a strong acid it is fully ionised so the concentration of the hydrogen is double the concentration of the acid
- This would mean that 0.1 mol dm^{-3} would be 0.2 mol dm^{-3} in $[H^+]$ and have a pH of 0.69
- However, measurements of the pH of 0.1 mol dm^{-3} sulfuric acid show that it is actually about pH 0.98, which indicates it is not fully ionised
- The ionisation of sulfuric acid occurs in two steps

$$H_2SO_4 \rightarrow HSO_4^- + H^+$$

$$HSO_4^- \rightleftharpoons SO_4^{2-} + H^+$$

- Although the first step is thought to be fully ionised, the second step is suppressed by the abundance of hydrogen ions from the first step creating an equilibrium
- The result is that the hydrogen ion concentration is less than double the acid concentration

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Weak acids

The pH of **weak acids** can be calculated when the following is known: The **concentration** of the acid The K_a value of the acid From the K_a expression we can see that there are three variables:

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

- However, the equilibrium concentration of $[H^+]$ and $[A^-]$ will be the same since one molecule of HA dissociates into one of each ion
- This means you can simplify and re-arrange the expression to

$$K_a \times [HA] = [H^+]^2$$

$$[H^+]^2 = K_a \times [HA]$$

- Taking the square roots of each side

$$[H^+] = \sqrt{(K_a \times [HA])}$$

- Then take the negative logs

$$pH = -\log[H^+] = -\log\sqrt{(K_a \times [HA])}$$

Worked Example

pH calculations of weak acids

Calculate the pH of 0.100 mol dm^{-3} ethanoic acid at 298 K.

$K_a = 1.74 \times 10^{-5}$ mol dm^{-3}

Answer

Ethanoic acid is a weak acid which ionises as follows:

$$CH_3COOH\ (aq) \rightleftharpoons H^+\ (aq) + CH_3COO^-\ (aq)$$

Step 1: Write down the equilibrium expression to find K_a

$$K_a = \frac{[H^+]\,[CH_3COO^-]}{[CH_3COOH]}$$

Step 2: Simplify the expression

- The ratio of H^+ to CH_3COO^- ions is 1:1
  - The concentration of H^+ and CH_3COO^- ions are therefore the same
  - The expression can be simplified to:

$$K_a = \frac{[H^+]^2}{[CH_3COOH]}$$

Step 3: Rearrange the expression to find $[H^+]$

$$[H^+] = \sqrt{K_a \times [CH_3COOH]}$$

Step 4: Substitute the values into the expression to find $[H^+]$

$$[H^+] = \sqrt{(1.74 \times 10^{-5}) \times [0.100]} = \mathbf{1.32 \times 10^{-3}\ mol\ dm^{-3}}$$

Step 5: Find the pH

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

$$\mathbf{pH = -\log(1.32 \times 10^{-3}) = 2.88}$$

Examiner Tips and Tricks

Assumptions

Sometimes exam questions will ask what assumptions are made in calculating the pH of a weak acid. There are two being made in these calculations.

1. We assume the concentration of the anion, $[A^-]$, is the same as $[H^+]$ when dissociation occurs, which is why we can simplify $[H^+][A^-]$ to $[H^+]^2$
2. We assume the concentration of $[HA]_{eqm}$ is the same as $[HA]_{initial}$, since the degree of dissociation is very small. In other words we say the dissociation of [HA] is negligible or so small it can be ignored.

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Ionic Product of Water, Kw

- 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:

$$H_2O\,(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

THE EQUILIBRIUM CONSTANT FOR THE REACTION IS,

$$K_c = \frac{[H^+][OH^-]}{[H_2O]}$$

$$K_c \times [H_2O] = [H^+][OH^-]$$

THE CONCENTRATION OF WATER IS CONSTANT, SO THE LEFT SIDE BECOMES:

$$K_w = [H^+][OH^-] = 1 \times 10^{-14}\,mol^2dm^{-6} \text{ AT } 298\,K$$

- This is a specific equilibrium constant called the **ionic product for water**
- The product of the two ion concentrations is *always* $\mathbf{1 \times 10^{-14}\,mol^2\,dm^{-6}}$
- This makes it straightforward to see the relationship between the two concentrations and the nature of the solution:

[H+] & [OH-] Table

$[H^+]$	$[OH^-]$	Type of solution
0.1	1×10^{-13}	acidic
1×10^{-3}	1×10^{-11}	acidic
1×10^{-5}	1×10^{-9}	acidic
1×10^{-7}	1×10^{-7}	neutral
1×10^{-9}	1×10^{-5}	alkaline
1×10^{-11}	1×10^{-3}	alkaline
1×10^{-13}	0.1	alkaline

The relationship between K_w and pK_w is given by the following equation:

$$pK_w = -\log K_w$$

Your notes

pH Calculation of a Strong Base

- **Strong bases** are completely **ionised** in solution

$$BOH\ (aq) \rightarrow B^+\ (aq) + OH^-\ (aq)$$

- Therefore, the concentration of hydroxide ions [OH^-] is **equal** to the concentration of base [BOH]
  - Even strong alkalis have small amounts of H^+ in solution which is due to the ionisation of water
- The concentration of OH^- in solution can be used to calculate the pH using the **ionic product of water**
- Once the [H^+] has been determined, the pH of the strong alkali can be founding using pH = -log[H^+]

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

$$[H^+] = \frac{1 \times 10^{-14}}{[OH^-]}$$

$$pH = -\log[H^+] = -\log\left(\frac{1 \times 10^{-14}}{[OH^-]}\right)$$

- Similarly, the ionic product of water can be used to find the concentration of OH^- ions in solution if [H^+] is known, simply by dividing K_w by the [H^+]

Worked Example

pH calculations of a strong alkali

Question 1:

Calculate the pH of 0.15 mol dm^{-3} sodium hydroxide, NaOH

Question 2:

Calculate the hydroxide concentration of a solution of sodium hydroxide when the pH is 10.50

Answer

Sodium hydroxide is a strong base which ionises as follows:

$$NaOH\,(aq) \rightarrow Na^{+}\,(aq) + OH^{-}\,(aq)$$

Answer 1:

The pH of the solution is:

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

$[H^+] = (1 \times 10^{-14}) \div 0.15 = 6.66 \times 10^{-14}$

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

$= -\log 6.66 \times 10^{-14}$ **= 13.17**

Answer 2

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

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

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

$[H^+] = 10^{-10.50}$

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

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

$K_w = [H^+]\,[OH^-]$

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

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

Since K_w is $1 \times 10^{-14}\ mol^2\ dm^{-6}$,

$[OH^-] = (1 \times 10^{-14}) \div (3.16 \times 10^{-11})$

$[OH^-] =$ **$3.16 \times 10^{-4}\ mol\ dm^{-3}$**

Your notes

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Analysing pH Data

Strong and weak acids

- The relative strengths of different acids can be determined by measuring the pH of equimolar aqueous solutions of the acids, at the same temperature
- The higher the value of the pH, the weaker the acid

pH of 0.100 mol dm^{-3} Aqueous Solutions of Various Acids at 298K

Formula of acid	pH of 0.100 mol dm^{-3} aqueous solution
HCl	1.00
$CHCl_2COOH$	1.14
$CH_2ClCOOH$	1.93
HCOOH	2.38
CH_3COOH	2.87
CH_3CH_2COOH	2.93

Strong and weak bases

pH of 0.100 mol dm^{-3} Aqueous Solutions of Various Bases at 298K

Your notes

Formula of base	pH of 0.100 mol dm^{-3} aqueous solution
NH_3	11.13
CH_3NH_2	11.82
$(CH_3)_2NH$	11.83
$CH_3CH_2NH_2$	11.84
$CH_3CH_2CH_2NH_2$	11.86
NaOH	13.00

- The higher the value of the pH, the stronger the base

Salts

pH of 0.100 mol dm^{-3} Aqueous Solutions of Various Salts at 298K

Formula of salt	pH of 0.100 mol dm^{-3} aqueous solution
NaCl	7.00
KNO_3	7.00
CH_3COONa	8.88
NH_4Cl	5.13
CH_3COONH_4	7.00

- NaCl and KNO_3 both have pH's of 7.00 as they are made from a strong acid and a strong base
- CH_3COONa is alkaline as it is made of a weak acid (CH_3COOH) and a strong base (NaOH)
- NH_4Cl is acidic as it is made of a strong acid (HCl) and a weak base (NH_3)

- CH_3COONH_4 is neutral as it is made from a weak acid (CH_3COOH) and a weak base (NH_3) which both have similar relative strengths

Your notes

Effect of dilution on the pH of aqueous solutions of acids

Strong acids

- As concentration decreases by a factor of 10 the pH increases by one unit

pH of Aqueous Solutions of Hydrochloric Acid at Different Concentrations at 298K

Concentration / mol dm^{-3}	pH
1.00×10^{0}	0.00
1.00×10^{-1}	1.00
1.00×10^{-2}	2.00
1.00×10^{-3}	3.00
1.00×10^{-4}	4.00

- Following this logic we would expect a concentration of 1.00×10^{-8} mol dm^{-3} to have a pH of 8
- This makes no sense as it would mean our acidic solution is alkaline
- However when we have solutions that are this dilute we can no longer ignore the contribution of hydrogen ions from the dissociation of water
- The hydrochloric acid with a concentration of 1.00×10^{-8} mol dm^{-3} would have a pH close to 7 as the contribution of hydrogen ions from the water is greater than that from the acid

Weak acids

- As concentration decreases by a factor of 10 the pH increases by a factor of around 0.5

pH of Aqueous Solutions of Ethanoic Acid at Different Concentrations at 298K

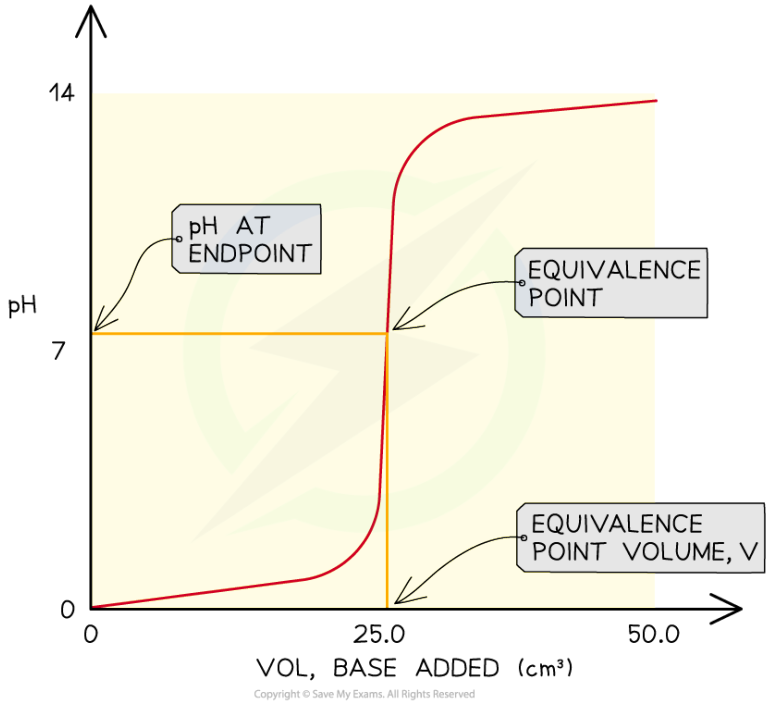
Concentration / mol dm^{-3}	pH
1.00×10^{0}	2.38
1.00×10^{-1}	2.88
1.00×10^{-2}	3.38
1.00×10^{-3}	3.88
1.00×10^{-4}	4.38

Your notes

Your notes

Titration Curves – Interpretation

- 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
- The result is characteristically shaped graph which can yield useful information about how the particular acid and alkali react together with stoichiometric information



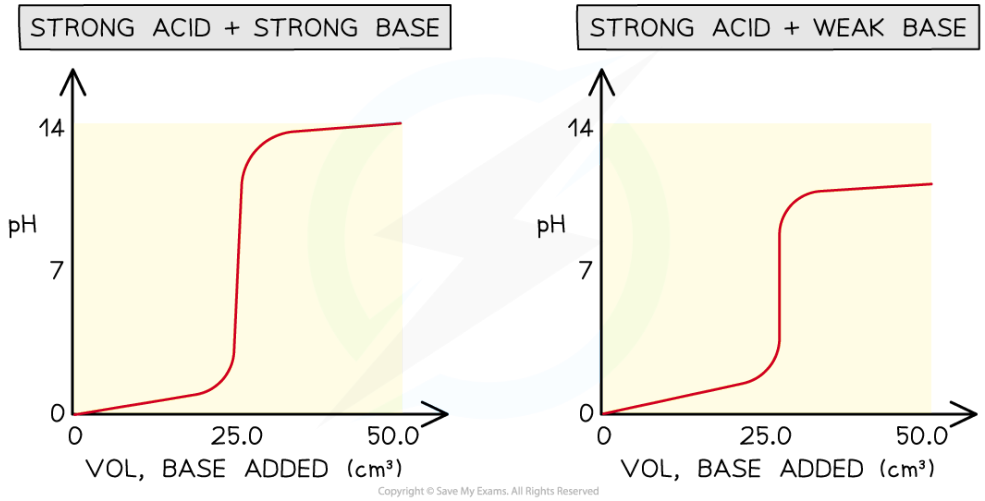
The features of a pH curve

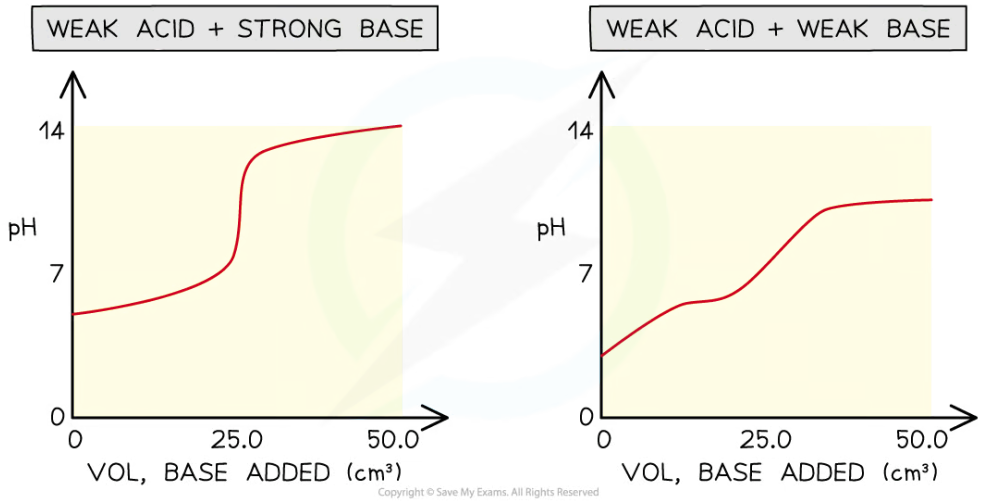
- All pH curves show an s-shape curve and the midpoint of the inflection is called the **equivalence** or **stochiometric point**
- From the curves you can
  - Determine the pH of the acid by looking where the curve starts on the y-axis
  - Find the pH at the equivalence point
  - Find volume of base 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
- strong acid + weak base
- weak acid + weak base

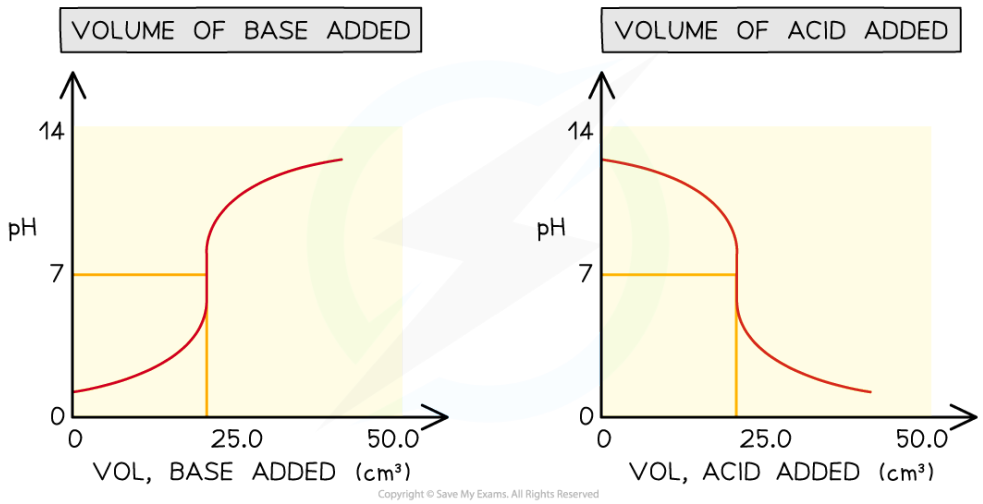




pH curves for the four types of acid-base titrations

- Without titles for the graph you can easily recognise which combination is shown by looking at the starting and ending pH and deducing whether the acid and alkali are strong or weak
- Sometimes you may see pH titration curves which show pH plotted against volume of acid added
- This produces the mirror image graph from which you can get all the same information

Your notes



Comparing different versions of pH titration curves

Choosing an Indicator

- Not all indicators are suitable for every type of titration
- Indicators behave like weak acids and form an equilibrium between two coloured species:

$$HA(\text{colour 1}) \rightleftharpoons H^+ + A^-(\text{colour 2})$$

- The equilibrium constant, K_a, for indicators, is known as K_{In} and is normally expressed in the logarithmic form, pK_{In}
- The working pH range of an indicator is a range of pH on either side of the pK_{In} value
- For example, the pK_{In} of methyl orange is 3.7
- Below pH 3.7 the dominant colour is colour 1 (red for methyl orange) and above it is colour 2 (yellow for methyl orange)
- The range of change for a weak acid-strong base titration is around pH 8–10
- Using methyl orange for this titration won't work because the range of change is far too high
  - You would see the indicator changing to yellow before you reach the end-point
- In this case, you need to use an indicator with a high pH range such as phenolphthalein

Examiner Tips and Tricks

The word base and alkali are being used interchangeably here, but you should know an alkali is a soluble base.Since we are dealing with titrations here, the bases are always in solution so they are also alkalis.

Your notes

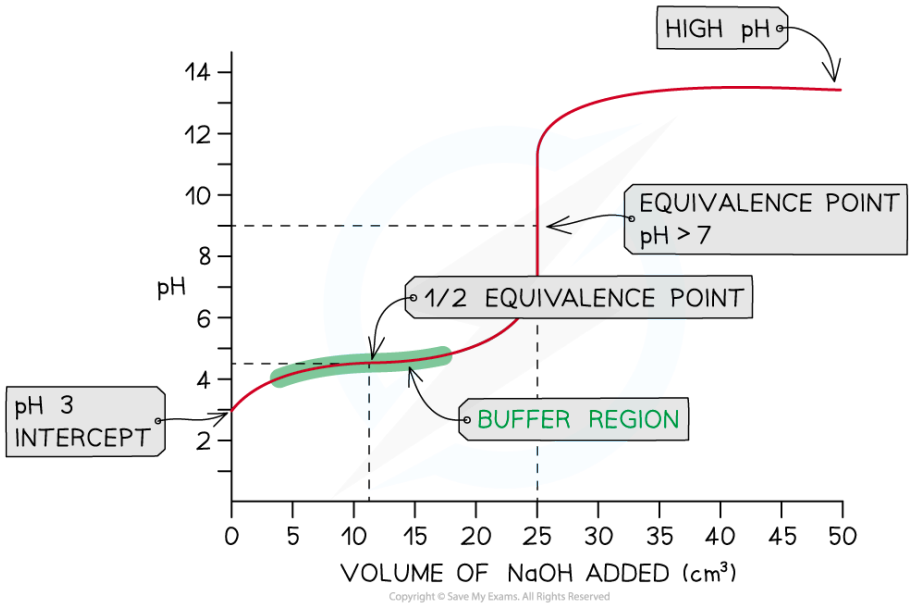
Titration Curves – Application

Your notes

- In this example, **strong** sodium hydroxide, NaOH (aq), is being added to **weak** ethanoic acid, CH_3COOH (aq)

$$\mathbf{NaOH\ (aq) + CH_3COOH\ (aq) \rightarrow CH_3COONa\ (aq) + H_2O\ (l)}$$

- 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
  - **$[CH_3COOH\ (aq)] = [CH_3COO^-\ (aq)]$**
  - At this point, it is important to note that the pK_a of the acid is equal to the pH
    - **pK_a = pH** at **half equivalence**
- The equivalence point in a weak acid - strong base titration is **above 7**



Weak acid – strong base pH curve

Your notes

Buffer Solutions – Action

- A **buffer solution** is a solution which resists changes in pH when small amounts of acids or alkalis are added
  - A buffer solution is used to keep the pH almost constant
  - A buffer can consists 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**

$$CH_3COOH\ (aq) \rightleftharpoons H^+\ (aq) + CH_3COO^-\ (aq)$$

Ethanoic acid	ethanoate ion
(high conc.)	(low conc.)

- Sodium ethanoate is a **salt** which fully ionises in solution

$$CH_3COONa\ (s) + aq \rightarrow Na^+\ (aq) + CH_3COO^-\ (aq)$$

Sodium ethanoate	ethanoate ion
(low conc.)	(high conc.)

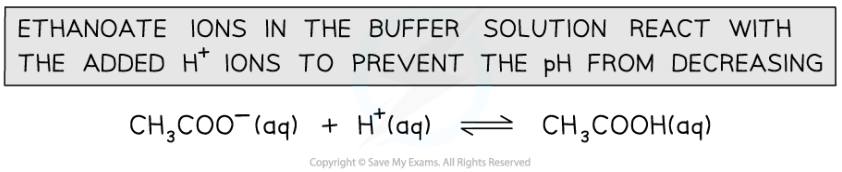
- There are **reserve supplies** of the acid (CH_3COOH) and its conjugate base (CH_3COO^-)
  - The buffer solution contains relatively high concentrations of CH_3COOH (due to partial ionisation of **ethanoic acid**) and CH_3COO^- (due to full ionisation of **sodium ethanoate**)
- In the **buffer solution**, the ethanoic acid is **in equilibrium** with hydrogen and ethanoate ions

$$CH_3COOH\ (aq) \rightleftharpoons H^+\ (aq) + CH_3COO^-\ (aq)$$

(high conc.)	(high conc.)

- **When H^+ ions are added:**
  - The equilibrium position shifts to the **left** as H^+ ions react with CH_3COO^- ions to form more CH_3COOH until equilibrium is **re-established**
  - As there is a large reserve supply of CH_3COO^- the concentration of CH_3COO^- in solution doesn't change much as it reacts with the added H^+ ions

- As there is a large reserve supply of CH_3COOH the concentration of CH_3COOH in solution doesn't change much as CH_3COOH is formed from the reaction of CH_3COO^- with H^+
- As a result, the pH remains reasonably constant



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

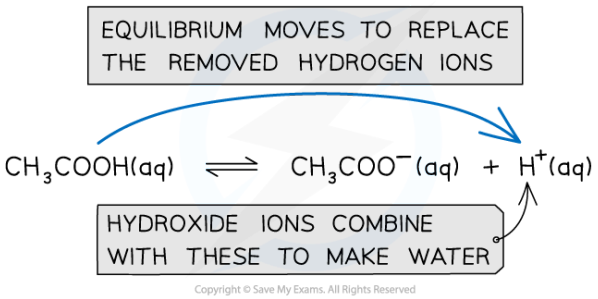
- **When OH^- ions are added:**
  - The OH^- reacts with H^+ to form water

$$OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$$

- The H^+ concentration **decreases**
  - The equilibrium position shifts to the right and more CH_3COOH molecules ionise to form more $H^+$and CH_3COO^- until equilibrium is re-established

$$CH_3COOH(aq) \rightarrow H^+(aq) + CH_3COO^-(aq)$$

- As there is a large reserve supply of CH_3COOH the concentration of CH_3COOH in solution doesn't change much when CH_3COOH dissociates to form more H^+ ions
  - As there is a large reserve supply of CH_3COO^- the concentration of CH_3COO^- in solution doesn't change much
  - As a result, the pH remains reasonably constant



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

Your notes

Worked Example

Your notes

Which of these mixtures would form a buffer solution with a pH **below** 7?

□	**A**	NaOH (aq) and excess HCl (aq)
□	**B**	NaOH (aq) and excess CH_3COOH (aq)
□	**C**	excess NaOH (aq) and HCl (aq)
□	**D**	excess NaOH (aq) and CH_3COOH (aq)

Answer:

- **B** / NaOH (aq) and excess CH_3COOH (aq)

This is because:

- A buffer with a pH lower than 7 can be made from a weak acid and its salt or by **partial neutralisation** of a weak acid
- **B** contains a weak acid that is in excess and NaOH, so the weak acid will be partially neutralised leaving a solution that contains a weak acid and its conjugate base - this is a buffer solution
- All of the other options are incorrect because the solutions would not form a buffer

Buffer Solutions – Applications

Controlling the pH of blood

- In humans, HCO_3^- ions act as a buffer to keep the blood pH between 7.35 and 7.45
- Body cells produce CO_2 during **aerobic respiration**
- This CO_2 will combine with water in blood to form a solution containing H^+ ions

$$CO_2\,(g) + H_2O\,(l) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq)$$

- This equilibrium between CO_2 and HCO_3^- is extremely important
- If the concentration of H^+ ions is not regulated, the blood pH would drop and cause '**acidosis**'
  - **Acidosis** refers to a condition in which there is too much acid in the body fluids such as blood
  - This could cause body malfunctioning and eventually lead to coma
- **If there is an increase in H^+ ions**
- The equilibrium position shifts to the **left** until equilibrium is restored

$$CO_2\,(g) + H_2O\,(l) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq)$$

- This reduces the concentration of H^+ and keeps the pH of the blood **constant**

- **If there is a decrease in H^+ ions**
  - The equilibrium position shifts to the **right** until equilibrium is restored

$$CO_2\,(g) + H_2O\,(l) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq)$$

- This increases the concentration of H^+ and keeps the pH of the blood **constant**

Buffers in food

- A combination of various factors such as light, heat, oxygen and various kinds of microorganisms can spoil food
  - We try to reduce this by keeping food in airtight containers and/or in refrigerators
- Microorganisms spoiling food depends on the pH value of the food.
- Most microorganisms thrive when the pH of their surroundings is around neutral (pH 6.6 - 7.5)
- Most bacteria can survive at pH values as low as 4.4 and as high as 9.0
- An important factor in whether food spoils is its **buffer capacity**
  - The buffer capacity of food is a measure of the amount of acid or base required to significantly change the pH of the food
- The more protein there is in the food, the higher the buffer capacity
  - This is because the amino acids present have both acidic and basic properties
  - This means it takes longer for the pH of the food to change enough for the bacteria to begin to multiply

Your notes

Your notes

Buffer Calculations

- The pH of a **buffer solution** can be calculated using:
  - The K_a of the **weak acid**
  - The **equilibrium concentration** of the **weak acid** and its **conjugate base** (salt)
- To determine the pH, the concentration of **hydrogen ions** is needed which can be found using the equilibrium expression

$$K_a = \frac{[salt]\,[H^+]}{[acid]} \text{ which can be rearranged to } [H^+] = K_a \times \frac{[acid]}{[salt]}$$

- To simplify the calculations, **logarithms** are used such that the expression becomes:

$$-\log_{10}[H^+] = -\log_{10} K_a \times -\log_{10} \frac{[acid]}{[salt]}$$

- Since $-\log_{10}[H^+] = pH$, the expression can also be rewritten as:

$$pH = pK_a + \log_{10} \frac{[salt]}{[acid]}$$

- This is known as the Hendersen-Hasselbalch equation

Worked Example

Calculate the pH of a buffer solution containing 0.305 mol dm^{-3} of ethanoic acid and 0.520 mol dm^{-3} sodium ethanoate.

The K_a of ethanoic acid $= 1.74 \times 10^{-5}$ mol dm^{-3} at 298 K

Answer

Ethanoic acid is a weak acid that ionises as follows:

$$CH_3COOH\,(aq) \rightleftharpoons H^+\,(aq) + CH_3COO^-\,(aq)$$

Step 1: Write down the equilibrium expression to find K_a

$$K_a = \frac{[CH_3COO^-]\,[H^+]}{[CH_3COOH]}$$

Your notes

Step 2: Rearrange the equation to find [H⁺]

$$[H^+] = K_a \times \frac{[CH_3COOH]}{[CH_3COO^-]}$$

Step 3: Substitute the values into the expression

$$[H^+] = 1.74 \times 10^{-5} \times \frac{0.305}{0.520}$$

$$= 1.02 \times 10^{-5} \text{ mol dm}^{-3}$$

Step 4: Calculate the pH

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

$$= -\log 1.02 \times 10^{-5}$$

$$= 4.99$$

How to make a buffer solution with a required pH

- To make a buffer solution with a pH of less than 7, you need to use a mixture of a weak acid and its conjugate base
  - Conversely, you can make a buffer solution with a pH greater than 7 by using a mixture of a weak base and its conjugate acid
- Imagine we want to make a buffer solution with a pH of 5.00 at a temperature of 298K
- This would require a hydrogen ion concentration of:

$$[H+(aq)] = 1.00 \times 10^{-5} \text{ mol dm}^{-3}$$

- The hydrogen ion concentration of a buffer solution of a weak acid and its conjugate base is calculated using the formula:

$$[H^+(aq)] = K_a \times \frac{[\text{acid}]}{[\text{base}]}$$

- We will use ethanoic acid as our weak acid of choice, with a K_a value of 1.74×10^{-5} mol dm^{-3}
- Substituting our known values into the equation we get:

$$1.00 \times 10^{-5} = 1.74 \times 10^{-5} \times \frac{[\text{acid}]}{[\text{base}]}$$

- This gives a value for the ratio of the concentrations of acid and base needed in our buffer solution:

$$\frac{[\text{acid}]}{[\text{base}]} = 0.575$$

- Mixing an equal volume of ethanoic acid with a concentration of 0.575 mol dm^{-3} and a sodium ethanoate solution of 1.00 mol dm^{-3} would allow us to make this buffer solution
- This would give a solution with an acid concentration of 0.2875 mol dm^{-3} and a salt concentration of 0.500 mol dm^{-3}

$$\frac{0.2875}{0.500} = 0.575$$

Your notes