Edexcel

A - Level

Chemistry

CODE: (WCH11)

Topic 14

Acid base equilibria

BRØNSTED-LOWRY ACIDS AND BASES

In 1923, physical chemists Johannes Nicolaus Brønsted in Denmark and Thomas Martin Lowry in England independently proposed the theory that carries their names. In the Brønsted- Lowry theory, acids and bases are defined by the way they react with each other.

▲ **fig A** Johannes Nicolaus Brønsted (1879 -1947).

▲ **fig B** Thomas Martin Lowry (1874-1936).

They defined an acid as a substance that can donate a proton, i.e. a **proton donor** (hydrogen ion, H+). They defined a base as a substance that can accept a proton, i.e. a **proton acceptor.**

CONJUGATE ACID-BASE PAIRS

An equilibrium is established when hydrogen chloride dissolves in water. The following equation represents this equilibrium:

$$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

In the forward reaction:

- HCl is acting as an acid because it is donating a proton to H_2O.
- H_2O is behaving as a base as it is accepting a proton from HCl.

In the reverse reaction:

- H_3O^+ is behaving as an acid because it is donating a proton to Cl^-.
- Cl^- is behaving as a base because it is accepting a proton from H_3O^+.

So the equilibrium mixture above contains two conjugate acid- base pairs:

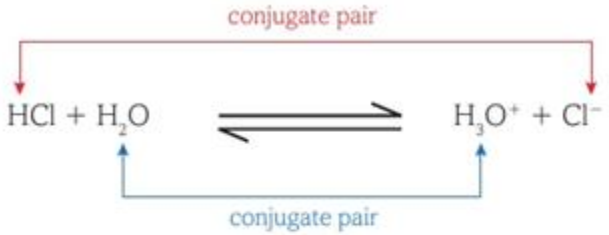


fig C Conjugate acid–base pairs formed from hydrochloric acid and water.

Cl- is the **conjugate base** of HCl; H2O is the conjugate base of H_3O+.

Hydrochloric acid can donate one proton - it is called a monoprotic or monobasic acid.
Sulfuric acid can donate two protons and is therefore called a diprotic or dibasic acid.

Step 1: $H_2SO_4 \rightarrow H^+ + HSO_4^-$

Step 2: $HSO_4^- \rightarrow H^+ + SO_4^{2-}$

Similarly, some bases such as the carbonate ion can accept more than one proton:

Step 1: $CO_3^{2-} + H^+ \rightarrow HCO_3^-$

Step 2: $HCO_3^- + H^+ \rightarrow H_2CO_3$

The carbonate ion is therefore described as a *diprotic* or diacidic base.

ANOTHER EXAMPLE OF A CONJUGATE ACID-BASE PAIR

An equilibrium is established when ammonia dissolves in water. The following equation represents this equilibrium:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

In the forward reaction:

- NH_3 is acting as a base because it is accepting a proton from H_2O.
- H_2O is acting as an acid because it is donating a proton to NH_3.

In the reverse reaction:

- NH_4^+ is behaving as an acid because it is donating a proton to OH^-.
- OH^- is behaving as a base because it is accepting a proton from NH_4^+.

So the equilibrium contains two acid–base conjugate pairs:

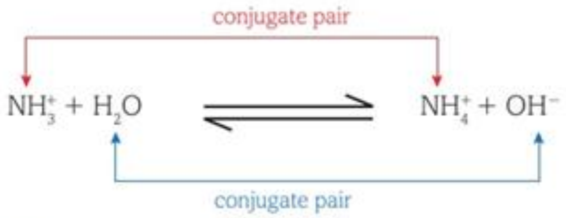


fig D Conjugate acid–base pairs formed from ammonia and water.

AMPHOTERIC SUBSTANCES

In its reaction with HCl, H_2O behaves as a base by accepting a proton. However, in its reaction with NH_3, H_2O behaves as an acid by donating a proton.
A substance that can act as either an acid or a base is described as being **amphoteric**.

NITRIC ACID AS A BASE

The most common method to nitrate benzene (see Topic 18) is to use the 'nitrating mixture' of concentrated nitric acid and concentrated sulfuric acid. This mixture forms the equilibrium: HSO + HNO

$$\underset{\text{Acid 1}}{H_2SO_4} + \underset{\text{Base 2}}{HNO_3} \rightleftharpoons \underset{\text{Base 1}}{HSO_4^-} + \underset{\text{Acid 2}}{H_2NO_3^+}$$

In this reaction:

- H_2SO_4 is an acid; its **conjugate base** is HSO_4^-
- HNO_3 is a base; its **conjugate acid** is $H_2NO_3^+$.

It seems strange to refer to nitric acid as a base. However, in this reaction the nitric acid is behaving as a base.

STRONG AND WEAK ACIDS

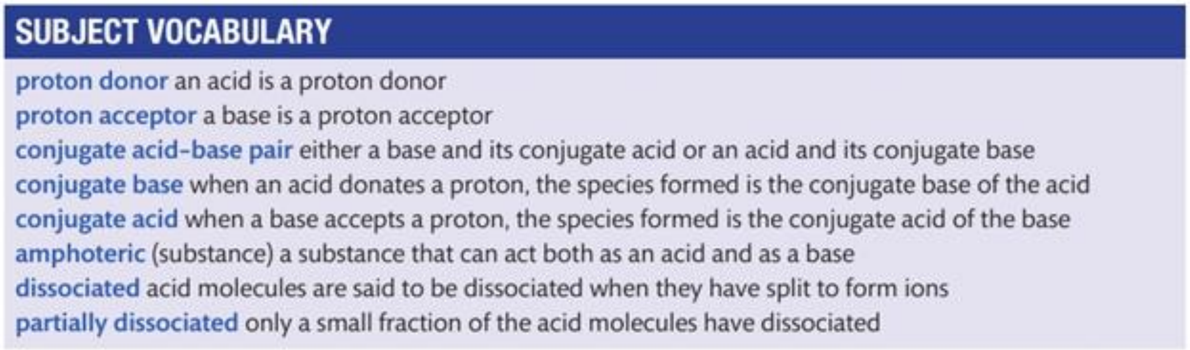
A strong acid is defined as one that is almost completely dissociated in aqueous solution.
Virtually all the hydrogen chloride molecules are dissociated in a dilute solution of hydrochloric acid. We usually represent this by using a single direction arrow in the equation for the dissociation:

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

By contrast, a weak acid is defined as one that is only partially dissociated (often less than 10%) in aqueous solution. Organic acids such as ethanoic acid are typically weak acids.

We represent partial dissociation by using the reversible arrow sign ($\rightleftharpoons$) in the equation for the dissociation:

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



SUBJECT VOCABULARY

proton donor	an acid is a proton donor
proton acceptor	a base is a proton acceptor
conjugate acid-base pair	either a base and its conjugate acid or an acid and its conjugate base
conjugate base	when an acid donates a proton, the species formed is the conjugate base of the acid
conjugate acid	when a base accepts a proton, the species formed is the conjugate acid of the base
amphoteric	(substance) a substance that can act both as an acid and as a base
dissociated	acid molecules are said to be dissociated when they have split to form ions
partially dissociated	only a small fraction of the acid molecules have dissociated

14A 2 HYDROGEN ION CONCENTRATION AND THE PH SCALE

HYDROGEN ION CONCENTRATION AND PH

STRONG ACIDS

As already mentioned, we assume strong acids are dissociated completely when they are dissolved in water. This means that the hydrogen ion concentration is related directly to the concentration of the acid.

CALCULATING HYDROGEN ION CONCENTRATION FROM PH

It is a simple matter to calculate the hydrogen ion concentration from a given pH value.
You should use the following equation:

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

WEAK ACIDS

Determining the hydrogen ion concentration of an aqueous solution of a weak acid is more complicated. This is because a significant amount of undissociated acid is present in solution. It is necessary to refer to the acid dissociation constant, K_a, for the acid.

ACID DISSOCIATION CONSTANT

If we use HA to represent a weak acid, then the equation for its dissociation in aqueous solution is:

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

When we apply the equilibrium law to this reaction we obtain:

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

This constant is called the acid dissociation constant and is given the symbol K_a.

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

$$K_a = \frac{[CH_3COO^-(aq)][H^+(aq)]}{[CH_3COOH(aq)]}$$

Every time a molecule of CH_3COOH dissociates, a CH_3COO^- ion and a H^+ ion are formed.

This means that $[CH_3COO^-(aq)] = [H^+(aq)]$.

So, the expression for K_a can be simplified to:

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

At this stage, it is important to recognise that the concentrations in the expression for K_a are the *equilibrium* concentrations. However, if the value of K_a is very small (as it is in this case) then the concentration of the undissociated acid at equilibrium is very similar to the initial concentration of the acid. It is therefore reasonable to say the concentration at equilibrium is the same as the initial concentration.

Therefore,

$$K_a = \frac{[H^+(aq)]^2}{0.0500} = 1.74 \times 10^{-5}\,\text{mol dm}^{-3}$$

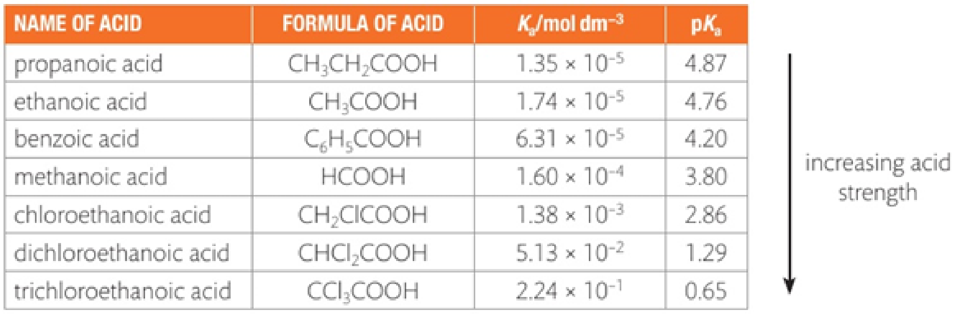
$$[H^+(aq)] = \sqrt{(0.0500 \times 1.74 \times 10^{-5})} = 9.33 \times 10^{-4}\,\text{mol dm}^{-3}$$

This gives a pH of 3.03.

K_a AND Pk_a, VALUES

Table A (next page) lists some weak monobasic organic acids together with their K_a AND Pk_a, values at 298 K, where:

$$pK_a = -\lg K_a$$



NAME OF ACID	FORMULA OF ACID	K_a/mol dm^{-3}	pK_a
propanoic acid	CH_3CH_2COOH	1.35×10^{-5}	4.87
ethanoic acid	CH_3COOH	1.74×10^{-5}	4.76
benzoic acid	C_6H_5COOH	6.31×10^{-5}	4.20
methanoic acid	$HCOOH$	1.60×10^{-4}	3.80
chloroethanoic acid	$CH_2ClCOOH$	1.38×10^{-3}	2.86
dichloroethanoic acid	$CHCl_2COOH$	5.13×10^{-2}	1.29
trichloroethanoic acid	CCl_3COOH	2.24×10^{-1}	0.65

table A

CALCULATING THE PH OF A DIBASIC ACID

Sulfuric acid is the most common dibasic acid. It dissociates in two stages:

$$H_2SO_4(aq) \rightarrow H^+(aq) + HSO_4^-(aq)$$

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

H_2SO_4 is a strong acid and is therefore fully dissociated. HSO_4^- is a weak acid ($K_a = 0.0100$ mol dm^{-3}.)

In a 0.500 mol dm^{-3} aqueous solution of H_2SO_4 the contribution to the [H^+(aq)] from the H_2SO_4 will be 0.500 mol dm^{-3}. If we assume that the contribution to the [H^+(aq)] from the HSO_4^- ion is x mol dm^{-3}, then we have the following relationship:

$$K_a\,(HSO_4^-) = 0.0100 = (0.500 - x)x/0.500$$

Solving this quadratic equation gives $x = 0.0098$.

This gives a total [H^+(aq)] of 0.05098 mol dm^{-3} with a subsequent pH of 0.293.

SUBJECT VOCABULARY

pH (of an aqueous solution) the reciprocal of the logarithm to the base 10 of the hydrogen ion concentration, measured in moles per cubic decimetre, $pH = -\lg [H^+]$. This definition is difficult to remember, so either of the two equations given on page 83 can be used to define pH

pK_a $= -\lg K_a$

14A 3 Ionic product of water , K_W

DISSOCIATION OF WATER

Pure water has a slight electrical conductivity, so it must contain some ions. It self-ionises according to the following equation:

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

If we apply the equilibrium law to this reaction we obtain:

$$\frac{[H^+(aq)][OH^-(aq)]}{[H_2O(l)]} = \text{a constant}$$

As $[H_2O(l)]$ is constant at a given temperature, the expression may be simplified to:

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

This constant is called the **ionic product of water** and is given the symbol K_w.

The value of K_w at 298 K is $1.00 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$.

A neutral solution is defined as one in which the hydrogen ion concentration is equal to the hydroxide ion concentration. This is the case for pure water.

At 298 K, $[H^+(aq)] = 1.00 \times 10^{-7}\ \text{mol dm}^{-3}\ [(1.00 \times 10^{-14})^{1/2}]$

So, the pH of pure water at 298 K is 7.00 $[-\lg (1.00 \times 10^{-7})]$

K_w AND pK_w

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

$$pK_w = -\lg K_w$$

At 298 K, when $K_w = 1.00 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$, $pK_w = 14.00$

Table A gives the values of K_w and pK_w at various temperatures.

TEMPERATURE/K	273	283	293	303	313
K_w/mol² dm⁻⁶	1.14×10^{-15}	2.93×10^{-15}	6.81×10^{-15}	1.47×10^{-14}	2.92×10^{-14}
pK_w	14.94	14.53	14.17	13.83	13.53

table A

pH OF AQUEOUS SOLUTIONS OF STRONG BASES

An acid dissolved in water produces so many hydrogen ions that the small contribution from the water is insignificant, unless the acid concentration is very small.

However, even the most alkaline solutions contain some hydrogen ions because water ionises.

Sodium hydroxide is a strong base, so in dilute aqueous solutions we can consider its ions to be completely dissociated.

14A 4 Analyzing data from pH measurements

COMPARING SOLUTIONS THROUGH pH MEASUREMENT

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.

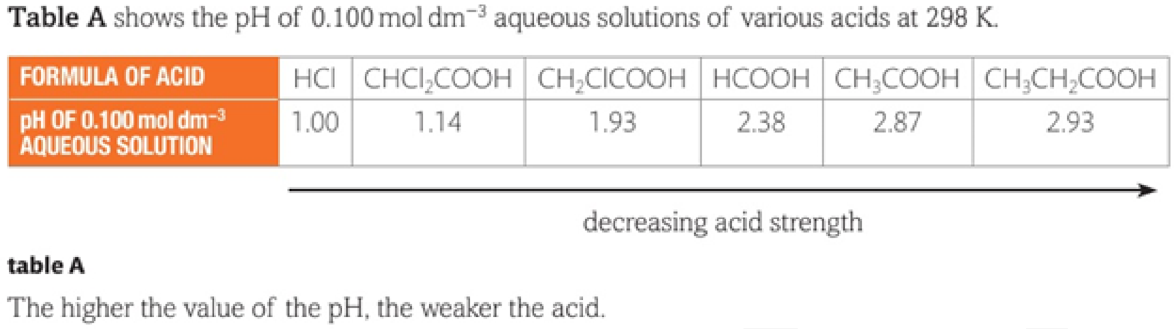


Table A shows the pH of 0.100 mol dm^{-3} aqueous solutions of various acids at 298 K.

FORMULA OF ACID	HCl	$CHCl_2COOH$	$CH_2ClCOOH$	HCOOH	CH_3COOH	CH_3CH_2COOH
pH OF 0.100 mol dm^{-3} AQUEOUS SOLUTION	1.00	1.14	1.93	2.38	2.87	2.93

decreasing acid strength →

table A

The higher the value of the pH, the weaker the acid.

STRONG AND WEAK BASES

The same method can be used to determine the relative strengths of bases.
Table B shows the pH of 0.100 mol dm3 aqueous solutions of various bases at 298 K.

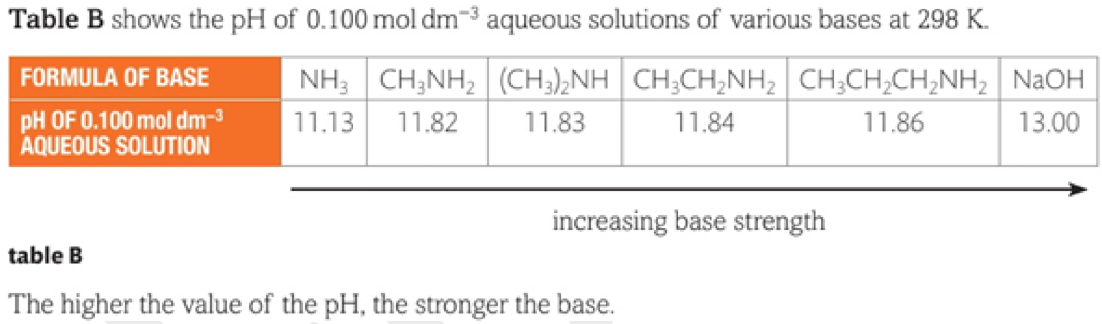


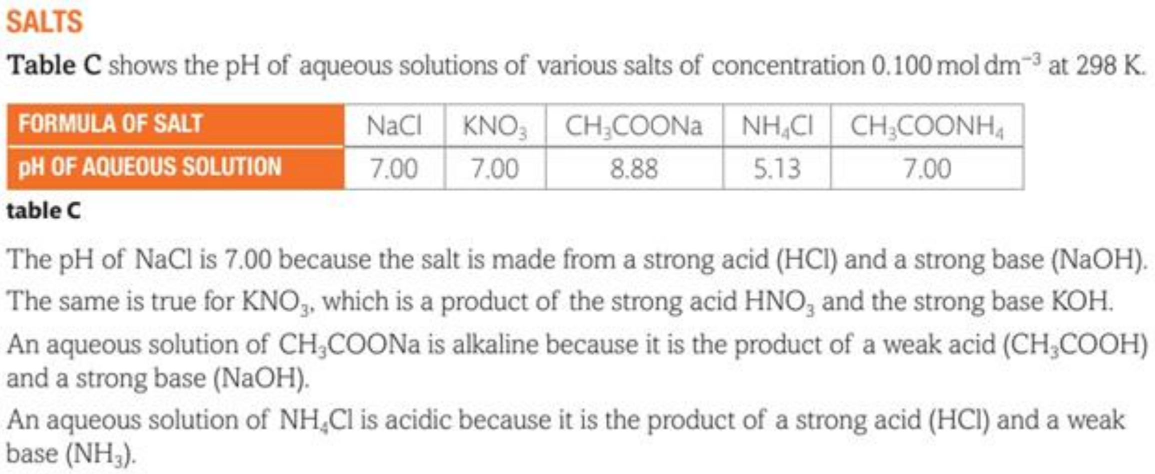
Table B shows the pH of 0.100 mol dm^{-3} aqueous solutions of various bases at 298 K.

FORMULA OF BASE	NH_3	CH_3NH_2	$(CH_3)_2NH$	$CH_3CH_2NH_2$	$CH_3CH_2CH_2NH_2$	NaOH
pH OF 0.100 mol dm^{-3} AQUEOUS SOLUTION	11.13	11.82	11.83	11.84	11.86	13.00

increasing base strength →

table B

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



SALTS

Table C shows the pH of aqueous solutions of various salts of concentration 0.100 mol dm^{-3} at 298 K.

FORMULA OF SALT	NaCl	KNO_3	CH_3COONa	NH_4Cl	CH_3COONH_4
pH OF AQUEOUS SOLUTION	7.00	7.00	8.88	5.13	7.00

table C

The pH of NaCl is 7.00 because the salt is made from a strong acid (HCl) and a strong base (NaOH). The same is true for KNO_3, which is a product of the strong acid HNO_3 and the strong base KOH.

An aqueous solution of CH_3COONa is alkaline because it is the product of a weak acid (CH_3COOH) and a strong base (NaOH).

An aqueous solution of NH_4Cl is acidic because it is the product of a strong acid (HCl) and a weak base (NH_3).

SUMMARY TABLE FOR AQUEOUS SOLUTIONS AT 298 K

SALT OF A STRONG ACID AND A STRONG BASE	pH = 7 (solution is neutral)
SALT OF A WEAK ACID AND A STRONG BASE	pH > 7 (solution is alkaline)
SALT OF A STRONG ACID AND A WEAK BASE	pH < 7 (solution is acidic)
SALT OF A WEAK ACID AND A WEAK BASE	pH depends on relative strengths of acid and base; if $K_a = K_b$, pH = 7 if $K_a > K_b$, pH < 7 if $K_a < K_b$, pH > 7

table D

EFFECT OF DILUTION ON THE pH OF AQUEOUS SOLUTIONS OF ACIDS

STRONG ACIDS

Table E shows the pH of five aqueous solutions of hydrochloric acid. In each case, the acid has been diluted by a factor of ten from 1.00 (1.00×10^0) to 0.000100 (1.00×10^{-4}) mol dm^{-3}. All solutions are at a temperature of 298 K.

CONCENTRATION/mol dm^{-3}	1.00 (1.00×10^0)	0.100 (1.00×10^{-1})	0.0100 (1.00×10^{-2})	0.00100 (1.00×10^{-3})	0.00100 (1.00×10^{-4})
pH	0.00	1.00	2.00	3.00	4.00

table E

The pH increases by one unit for a 10-fold decrease in concentration. Therefore, an aqueous solution of hydrochloric acid should have a pH of 8.00, which is nonsense. The pH of 10^{-8} mol dm-3 hydrochloric acid is close to 7, as the hydrogen ion concentration from water is greater than the acid.

WEAK ACIDS

Table F shows the pH of five aqueous solutions of ethanoic acid (CH_3COOH). In each case the acid has been diluted by a factor of ten from 1.00 (1.00×10^0) to 0.000100 (1.00×10^{-4}) mol dm^{-3}. Once again, all solutions are at a temperature of 298 K.

CONCENTRATION/mol dm^{-3}	1.00 (1.00×10^0)	0.100 (1.00×10^{-1})	0.0100 (1.00×10^{-2})	0.00100 (1.00×10^{-3})	0.000100 (1.00×10^{-4})
pH	2.38	2.88	3.38	3.88	4.38

table F

With a weak acid, the pH value increases by a factor of about 0.50 for each 10-fold decrease in concentration.

14B 1 Acid – Base titrations pH Curves and indicators

ACID-BASE TITRATIONS

END POINT AND EQUIVALENCE POINT

Acid-base titration involves mixing acids and bases in the correct proportions, known as the 'end point'. The equivalence point occurs when the acid and base react in the exact proportions, as per the stoichiometric equation. The pH at the **equivalence point** depends on the combination of acid and base used. For instance, a strong base like sodium hydroxide reacts with a weak acid like sodium chloride, resulting in a pH greater than 7. Conversely, a weak acid reacts with a strong base like ammonia.

TITRATION OF A STRONG ACID WITH A STRONG BASE

As you add an aqueous solution of an acid to an aqueous solution of a base, you might expect there to be a gradual change in the pH of the solution formed. This is not the case. When the pH of the solution is plotted against the volume of acid added, the shape of the curve depends on the nature of the acid and base used. The curves produced in this way are called 'pH titration curves'.

fig A A pH meter.

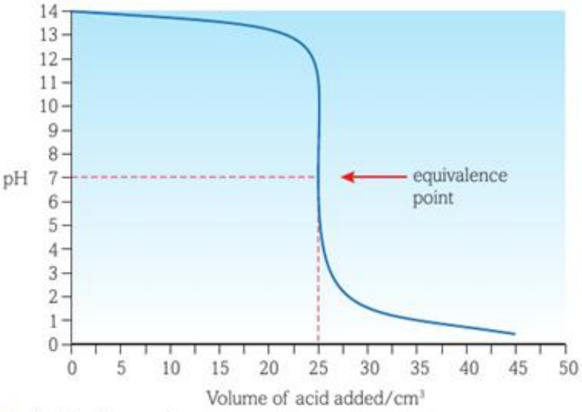


fig B pH curve for a strong acid–strong base titration.

TITRATION OF A WEAK ACID WITH A STRONG BASE

For this example we will add 1.00 mol dm3 ethanoic acid to 25 cm3 of 1.00 mol dm3 sodium hydroxide.

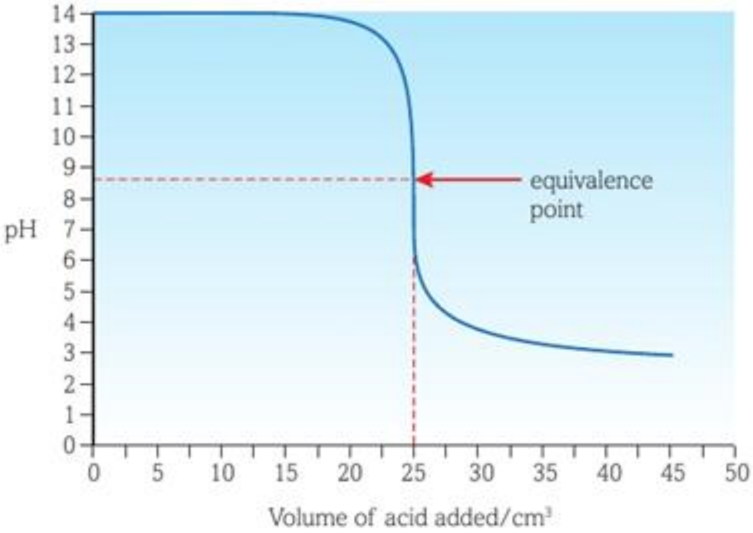


fig C pH curve for a weak acid–strong base titration.

TITRATION OF A STRONG ACID WITH A WEAK BASE

For this example we will add 1.00 mol dm^{-3} hydrochloric acid to 25 cm3 of 1.00 mol dm3 aqueous ammonia.

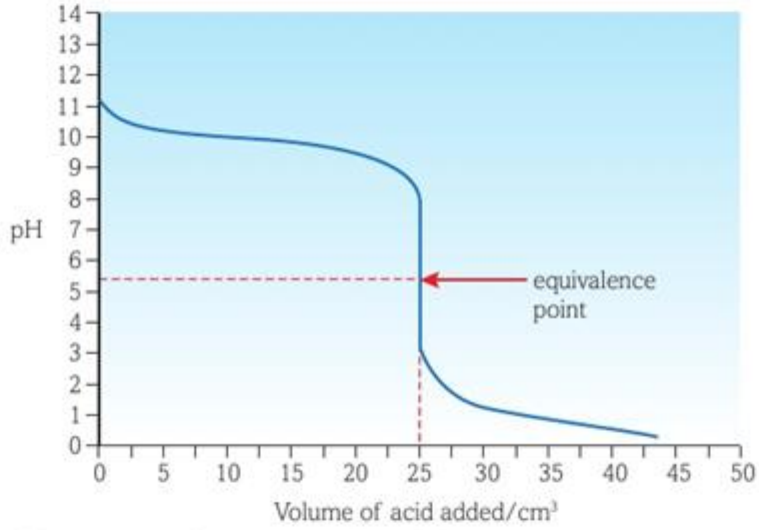


fig D pH curve for a strong acid–weak base titration.

TITRATION OF A WEAK ACID WITH A WEAK BASE

For this example we will add 1.00 mol dm^3 ethanoic acid to 25 cm^3 of 1.00 mol dm^3 aqueous ammonia.

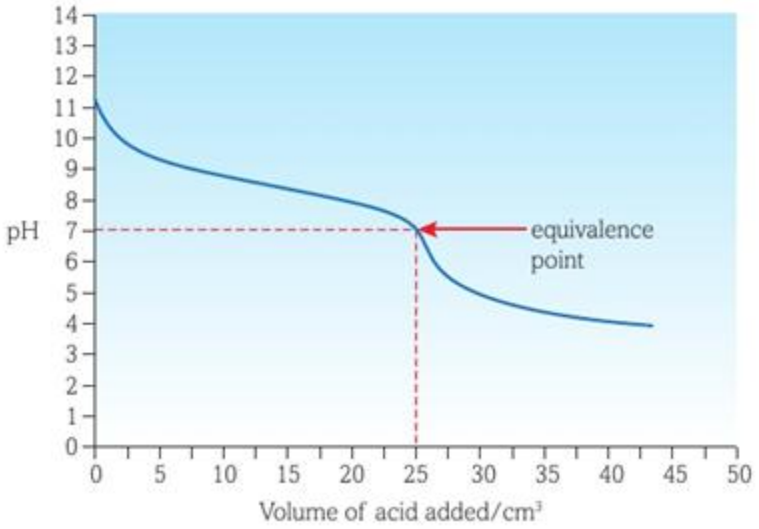


fig E pH curve for a weak acid–weak base titration.

ACID-BASE INDICATORS

Earlier in this section we looked at the pH titration curves obtained when an aqueous solution of an acid is added to an aqueous solution of a base. The four cases we considered were:

- strong acid-strong base
- weak acid-strong base
- strong acid-weak base
- weak acid-weak base.

We are now going to use these four curves to help us understand why different indicators are required for different types of
titrations.

An acid-base indicator is either a weak acid or a weak base. Most indicators are weak acids (HIn). For an indicator that is a weak acid, its dissociation in aqueous solution can be represented as:

$$HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$$

The molecule, Hin, and its conjugate base, In, have different colours in aqueous solution. For methyl orange, these are red and yellow, respectively:

$$\underset{\text{red}}{HIn(aq)} \rightleftharpoons H^+(aq) + \underset{\text{yellow}}{In^-(aq)}$$

There will be a stage at which [HIn(aq)] = [In⁻(aq)] and the indicator will appear orange. The exact pH at which this stage is reached can be determined using the equilibrium constant, K_{In}, for methyl orange.

$$K_{In} = \frac{[H^+(aq)][In^-(aq)]}{[HIn(aq)]} = 2.00 \times 10^{-4}\,mol\,dm^{-3}$$

When $[HIn(aq)] = [In^-(aq)]$, the expression becomes:

$$[H^+(aq)] = 2.00 \times 10^{-4}\,mol\,dm^{-3}$$

This gives a pH of 3.70 for the 'half-way' stage. So, methyl orange will change colour at a pH of 3.70.

PH RANGE OF INDICATORS

As a 'rule of thumb', the red colour of methyl orange will first predominate when $[HIn(aq)]$ is ten times $[In^-(aq)]$, and the yellow colour will predominate when $[In^-(aq)]$ is ten times $[HIn(aq)]$.

The approximate pH at which each colour predominates can be calculated as follows.

When $[HIn(aq)] = 10[In^-(aq)]$:

$$\frac{[H^+(aq)][In^-(aq)]}{10[In^-(aq)]} = 2.00 \times 10^{-4}\,mol\,dm^{-3}$$

$$[H^+(aq)] = 2.00 \times 10^{-3}\,mol\,dm^{-3}$$

So, the pH at which the red colour first predominates is 2.70.

Table A shows the pK_{In} values, pH ranges and colours of several common indicators.

INDICATOR	pK_{In}	pH RANGE	COLOUR	
			$HIn(aq)$	$In^-(aq)$
methyl orange	3.70	3.10–4.40	red	yellow
bromophenol blue	4.00	2.80–4.60	yellow	blue
bromothymol blue	7.00	6.00–7.60	yellow	blue
phenol red	7.90	6.80–8.40	yellow	red
phenolphthalein	9.30	8.20–10.00	colourless	red

table A

CHOICE OF INDICATOR

A good indicator shows a complete colour change upon the addition of one drop of acid from the burette. This is necessary in order to accurately determine the end point of the titration.

STRONG ACID-STRONG BASE TITRATION

Let us first of all consider the use of methyl orange and phenolphthalein as indicators for a strong acid-strong base titration.

Fig F shows the pH titration curve for 25 cm^3 of 1.00 mol dm^{-3} NaOH(aq) titrated with 1.00 mol dm^{-3} HCl(aq). The pH ranges of methyl orange and phenolphthalein have also been included.

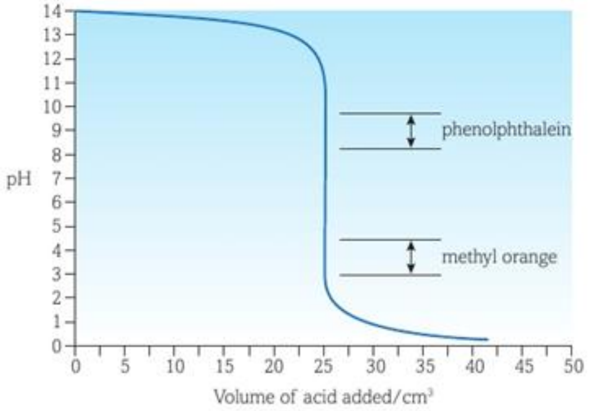


fig F Strong acid-strong base pH curve.

WEAK ACID-STRONG BASE TITRATION

We will now consider the suitability of each indicator for a weak acid-strong base titration.

Fig G shows the pH titration curve for 25 cm^3 of 1.00 mol dm^{-3} NaOH(aq) titrated with 1.00 mol dm^{-3} CH_3COOH(aq). Once again, the pH ranges of methyl orange and phenolphthalein have also been included.

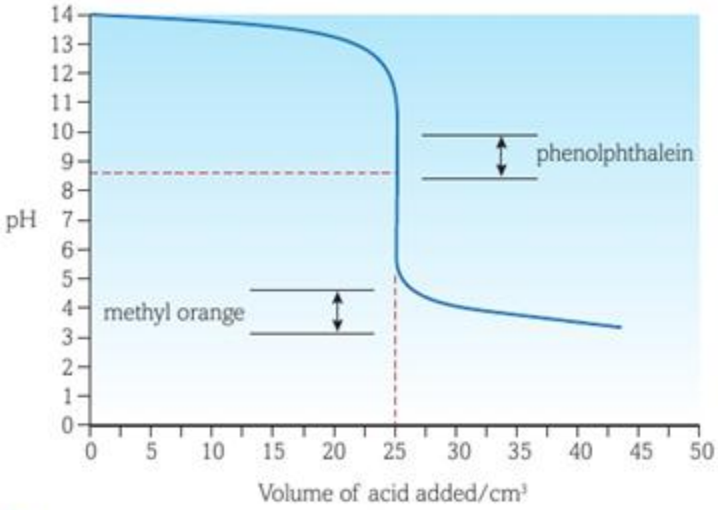
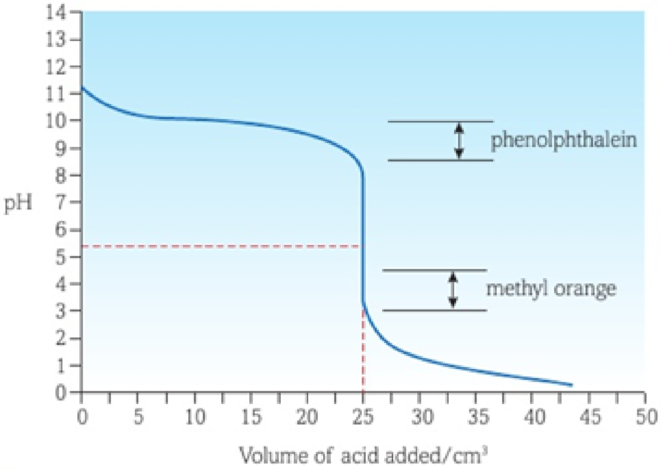


fig G Weak acid-strong base pH curve.

STRONG ACID-WEAK BASE TITRATION

Fig H shows the pH titration curve for 25 cm^3 of 1.00 mol dm^{-3} NH_3(aq) titrated with 1.00 mol dm^{-3} HCl(aq). Again, the pH ranges of methyl orange and phenolphthalein have also been included.

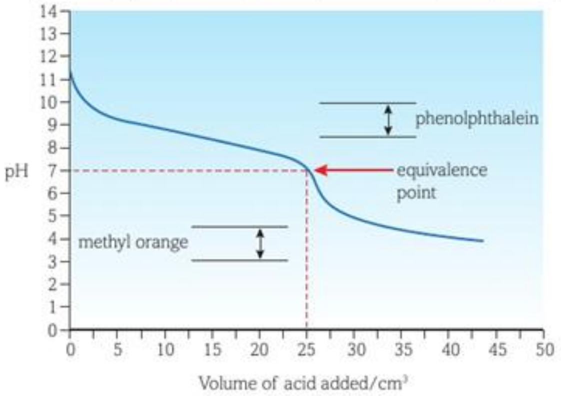


▲ **fig H** Strong acid-weak base pH curve.

This time, only the pH range of methyl orange falls within the steep section of the curve. So, methyl orange is suitable, but phenolphthalein is not.

WEAK ACID-WEAK BASE TITRATION

Fig I shows the pH titration curve for 25 cm^3 of 1.00 mol dm^{-3} NH_3(aq) titrated with 1.00 mol dm^{-3} CH_3COOH(aq). Again, the pH ranges of methyl orange and phenolphthalein have also been included.



▲ **fig I** Weak acid-weak base pH curve.

As there is no prominent steep section to the curve, neither indicator is suitable.

TITRATION CURVES WITH DIPROTIC ACIDS

A diprotic acid is an acid that produces two H+ ions per acid molecule.

A diprotic acid dissociates in water in two stages:

Stage 1: $H_2X(aq) \rightarrow H^+(aq) + HX^-(aq)$

Stage 2: $HX^-(aq) \rightarrow H^+(aq) + X^{2-}(aq)$

From the beginning of the reaction to the first equivalence point:

$$H_2X + NaOH \rightarrow NaHX + H_2O$$

From the first equivalence point to the second equivalence point:

$$NaHX + NaOH \rightarrow Na_2X + H_2O$$

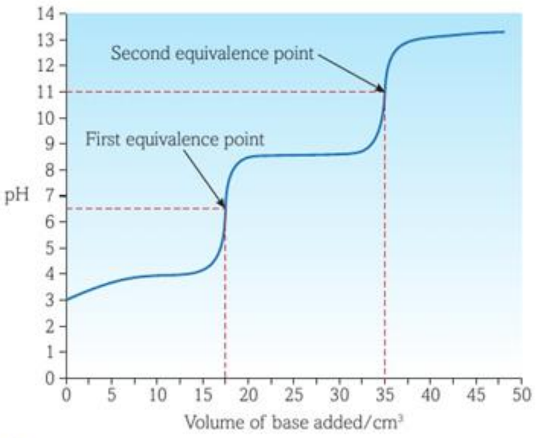
From the beginning of the reaction through to the second equivalence point (overall reaction):

$$H_2X + 2NaOH \rightarrow Na_2X + 2H_2O$$

At the first equivalence point, all H^+ ions from the first dissociation have reacted with NaOH.

At the second equivalence point, all H^+ ions from *both* reactions have reacted (twice as many as at the first equivalence point).

Therefore, the volume of NaOH added at the second equivalence point is exactly twice that at the first equivalence point.



▲ **fig J** Diprotic acid–strong base pH curve.

CHOOSING THE BEST INDICATOR

The best indicator to choose for a particular titration is the one whose pK_{in} value is as close as possible to the pH at the equivalence point.

Bromothymol blue (pK_{in} = 7.00) is a particularly good indicator for a strong acid-strong base titration.

SUBJECT VOCABULARY

equivalence point the point in a titration when the acid and base have reacted together in the exact proportions as dictated by the stoichiometric equation

14B 2 Buffer solutions

WHAT IS A BUFFER SOLUTION?

Many experiments, particularly in biochemistry, have to be performed in aqueous solutions of fairly constant pH. Unfortunately, it is impossible to make a solution whose pH is totally unaffected by the addition of even small amounts of acid or base. However, it is possible to make a solution whose pH remains almost unchanged when small amounts of acid or base are added. Such a solution is called a buffer solution.

There are many ways of making a buffer solution, but two of the most common are:

- to mix a weak acid with its conjugate base
- to mix a weak base with its conjugate acid.

BUFFER MADE FROM A WEAK ACID AND ITS CONJUGATE BASE

The simplest example of this is ethanoic acid and
sodium ethanoate. The salt of the weak acid has to be soluble in water, which is why sodium and potassium salts are commonly used to make buffer solutions.

In this mixture the acid is partially dissociated, whereas the salt is fully dissociated. The relevant equations are:

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

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

This mixture will produce a buffer solution with a pH less than 7. The exact pH depends on the concentration of both acid and its conjugate base, and can be calculated as follows.

CALCULATING THE PH OF A BUFFER SOLUTION

For our example we will use a solution that has been made by mixing equal volumes of 1.00 mol dm-3 ethanoic acid and 1.00 mol dm3 sodium ethanoate at 298 K.

If we assume that the extent of dissociation of the acid is negligible, then the concentration of CH_3COOH at equilibrium will be 0.500 mol dm^{-3}.

At 298 K,

$$K_a = \frac{[CH_3COO^-(aq)][H^+(aq)]}{[CH_3COOH(aq)]} = 1.74 \times 10^{-5}\ \text{mol dm}^{-3}$$

Rearranging this equation and substituting values for $[CH_3COOH(aq)]$ and $[CH_3COO^-(aq)]$ gives:

$$[H^+(aq)] = (1.74 \times 10^{-5} \times 0.500)/0.500\ \text{mol dm}^{-3}$$
$$= 1.74 \times 10^{-5}\ \text{mol dm}^{-3}$$

This gives a pH for the buffer solution of 4.76.

HOW DOES THE BUFFER ACTION WORK?

When a small amount of acid is added to the buffer solution, the majority of the H+ ions added react with the CH_3COO^- ions to form CH_3COOH molecules:

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

When a little base is added, the majority of the OH^- ions added react with the CH_3COOH molecules:

$$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$$

A new equilibrium mixture will be established in which the concentrations of both CH_3COOH and CH_3COO^- will have changed slightly from their original values. So, there will be a change in pH, but this will be minimal. This is shown by the following argument.

To show that the pH has changed very little, we once again need to make use of the expression for K_a of the acid:

$$K_a = \frac{[CH_3COO^-(aq)][H^+(aq)]}{[CH_3COOH(aq)]}$$

Rearranging this equation gives:

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

0.0100 mol of HCl will provide 0.0100 mol of H^+ ions. These will react with the CH_3COO^- ions in the buffer in a 1 : 1 molar ratio:

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

The amount of CH_3COOH present will now have increased from 0.500 to 0.510 mol.

The amount of CH_3COO^- present will have decreased from 0.500 to 0.490 mol.

So, the new concentrations of acid and base present are:

$$[CH_3COOH(aq)] = 0.510\ \text{mol dm}^{-3}$$

$$\text{and } [CH_3COO^-(aq)] = 0.490\ \text{mol dm}^{-3}$$

The new hydrogen ion concentration is given by:

$$[H^+(aq)] = 1.74 \times 10^{-5} \times \frac{0.510}{0.490} = 1.81 \times 10^{-5}\ \text{mol dm}^{-3}$$

The new pH = $-\lg(1.81 \times 10^{-5}) = 4.74$ (to 3 significant figures).

The pH has changed by 0.02 units from 4.76 to 4.74.

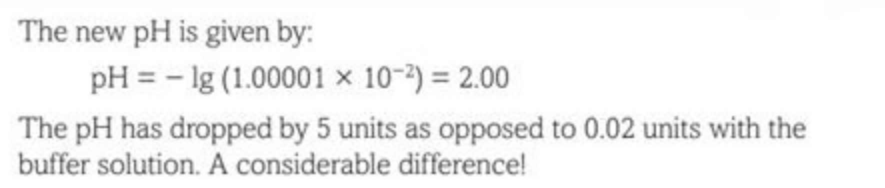
To understand how effective the buffer solution is in controlling the pH, let us consider adding 0.0100 mol of H^+ ions to 1 dm^3 of deionised water.

The pH, at 298 K, of deionised water is 7.00 so:

$$[H^+(aq)] = 1.00 \times 10^{7}\ \text{mol dm}^{-3}$$

Adding 0.0100 mol of H^+ ions gives:

$$[H^+(aq)] = (1.00 \times 10^{-7} + 0.0100) = 1.00001 \times 10^{-2}\ \text{mol dm}^{-3}$$



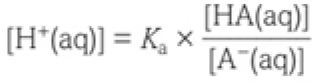
The new pH is given by:

$$pH = -\lg(1.00001 \times 10^{-2}) = 2.00$$

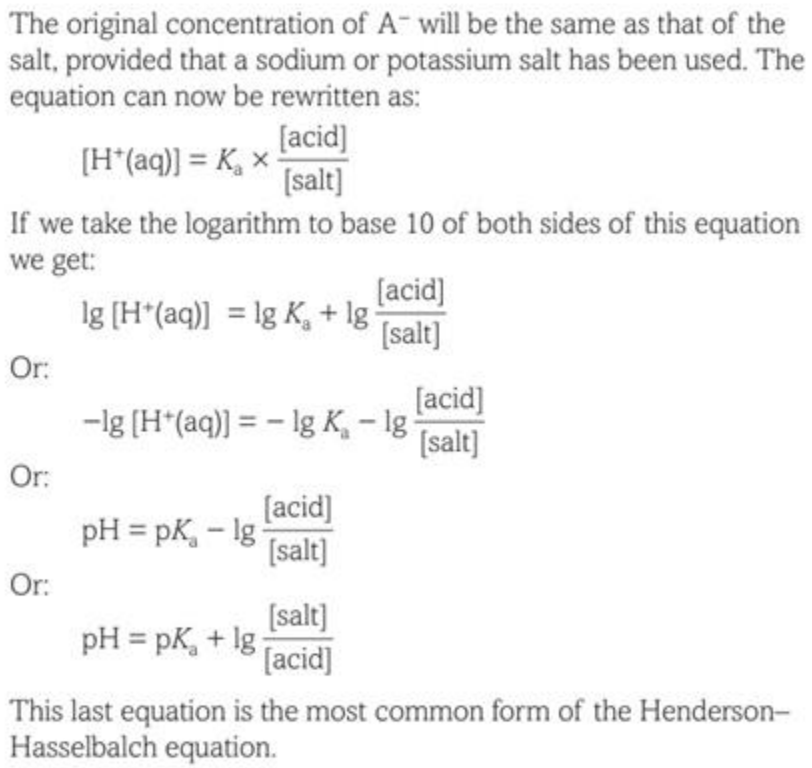
The pH has dropped by 5 units as opposed to 0.02 units with the buffer solution. A considerable difference!

HENDERSON-HASSELBALCH EQUATION

The Henderson-Hasselbalch equation can also be used to calculate the pH of a buffer solution.
For a weak acid, HA, and its conjugate base, A-, the following equation applies:



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



The original concentration of A^- will be the same as that of the salt, provided that a sodium or potassium salt has been used. The equation can now be rewritten as:

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

If we take the logarithm to base 10 of both sides of this equation we get:

$$\lg[H^+(aq)] = \lg K_a + \lg\frac{[acid]}{[salt]}$$

Or:

$$-\lg[H^+(aq)] = -\lg K_a - \lg\frac{[acid]}{[salt]}$$

Or:

$$pH = pK_a - \lg\frac{[acid]}{[salt]}$$

Or:

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

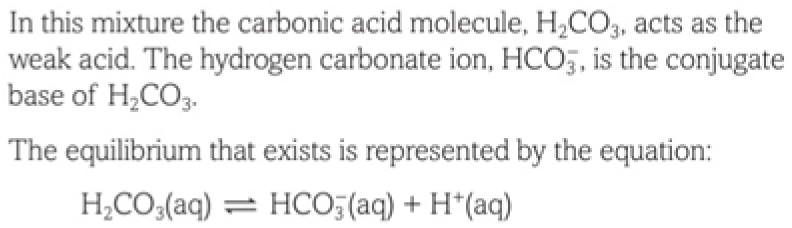
This last equation is the most common form of the Henderson–Hasselbalch equation.

HOW TO MAKE A BUFFER SOLUTION WITH A REQUIRED PH

To make a buffer solution with a pH less than 7, you need to use a mixture of a weak acid and its conjugate base.
In the opposite way, you need to use a mixture of a weak base and its conjugate acid to make a buffer solution with a pH greater than 7.

CONTROLLING THE PH OF BLOOD

The human body works within a narrow range of pH values. For example, the pH of arterial blood plasma needs to be in the range of 7.35 to 7.45. The way that the whole body functions would be affected if the pH of this blood plasma were to change significantly, particularly if it were to fall.
The pH of blood in cells is controlled by a mixture of buffers. The most important one is the carbonic acid-hydrogen carbonate buffer mixture.



In this mixture the carbonic acid molecule, H_2CO_3, acts as the weak acid. The hydrogen carbonate ion, HCO_3^-, is the conjugate base of H_2CO_3.

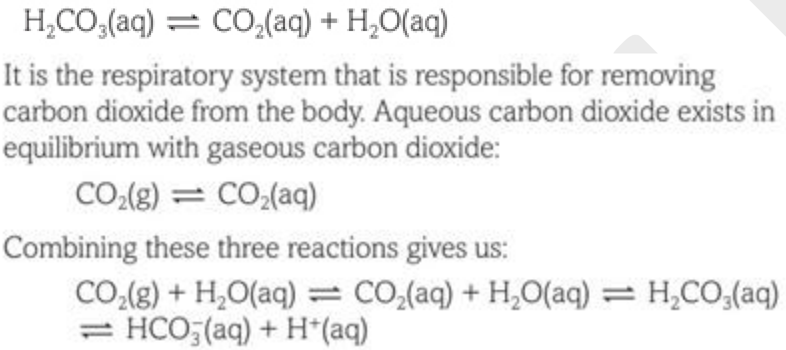
The equilibrium that exists is represented by the equation:

$$H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$$

Under normal circumstances, the amount of HCO_3 ion present is approximately 20 times that of H_2CO_3. As normal metabolism produces more acids than bases, this is consistent with the needs of the body.

Any increase in the concentration of hydrogen ions in the blood (for example, by the production of lactic acid in the muscles), results in the equilibrium shown above moving to the left as the added H+ ions react with the HCO3 ions. A variety of respiratory and metabolic factors can also cause the pH of the blood to rise.

This is considered to be the most important buffer because it is coupled with the respiratory system of the body. Carbonic acid is not particularly stable, and in aqueous solution it decomposes to form carbon dioxide and water:



$$H_2CO_3(aq) \rightleftharpoons CO_2(aq) + H_2O(aq)$$

It is the respiratory system that is responsible for removing carbon dioxide from the body. Aqueous carbon dioxide exists in equilibrium with gaseous carbon dioxide:

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

Combining these three reactions gives us:

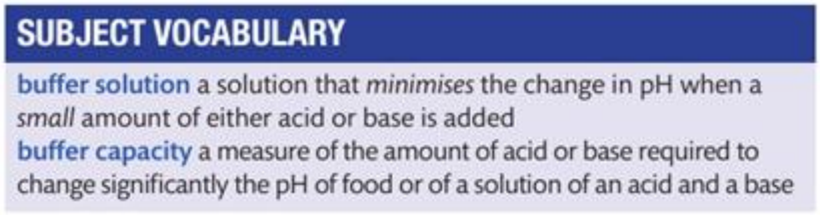
$$CO_2(g) + H_2O(aq) \rightleftharpoons CO_2(aq) + H_2O(aq) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$$

BUFFERS IN FOOD

A combination of various factors such as light, oxygen, heat, humidity and/or many kinds of microorganisms (bacteria and fungi) can spoil food. We try to reduce spoilage by keeping certain foods in the dark, in airtight containers and/or in refrigerators. Spoilage of food by microorganisms depends greatly on the pH value of the food.

Most microorganisms thrive when the pH of their surroundings is close to neutral (pH 6.6-7.5). The metabolism of these microorganisms is then greatest and they can multiply quickly. Most bacteria can survive at pH values as low as 4.4 and as high as 9.0. Only specialised bacteria can survive outside this range.

One important factor in the spoilage of food is its **buffer capacity.**



SUBJECT VOCABULARY

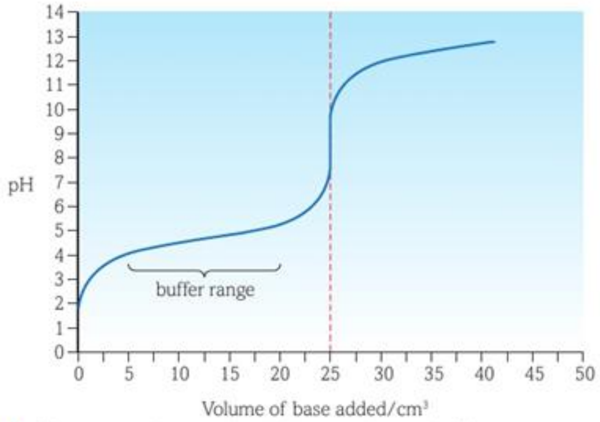
buffer solution a solution that *minimises* the change in pH when a *small* amount of either acid or base is added

buffer capacity a measure of the amount of acid or base required to change significantly the pH of food or of a solution of an acid and a base

14B 3 BUFFER SOLUTIONS AND PH CURVES

BUFFER ACTION DURING A TITRATION

Fig A shows a typical pH curve obtained when a weak acid is titrated against a strong base.



▲ **fig A** Strong base–weak acid pH curve showing buffer range.

DETERMINING K FROM A pH TITRATION CURVE

This experiment involves performing a titration with an aqueous solution of a weak acid in a conical flask. From a burette, we add a standard solution of a strong base, such as sodium hydroxide. We measure the pH of the solution after each addition.

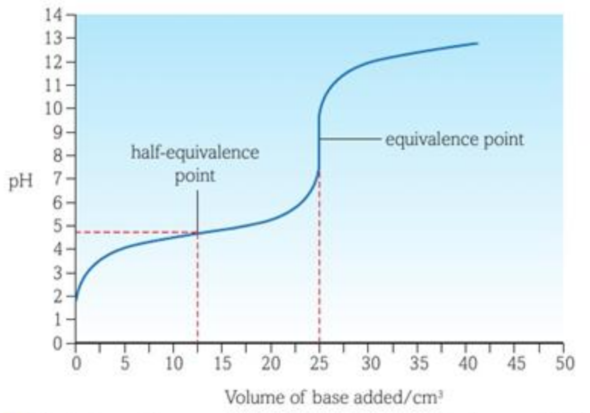
Then we are able to plot a graph of pH against volume of base added. From this graph we can determine the minimum volume of base required to completely react with all of the acid.

A typical pH titration curve is shown in **fig B**.

The volume at the equivalence point is 25 cm^3, so the volume at the half-equivalence point is 12.5 cm^3. The pH when 12.5 cm^3 of base is added is 4.80.

The pK_a of the acid = 4.80

K_a for the acid = $10^{-4.80} = 1.58 \times 10^{-5}\ mol\ dm^{-3}$



▲ **fig B** Strong base–weak acid pH curve showing equivalence and half-equivalence points.

SUPPORTING THEORY

The theoretical justification for determining K_a, for a weak acid by the method shown above is quite straightforward.

The mixture at the half-equivalence point is a buffer solution (as stated above). The pH of a buffer solution is calculated using the following equation:

$$\mathrm{pH} = \mathrm{p}K_a + \lg \frac{[\mathrm{salt}]}{[\mathrm{acid}]}$$

At the half-equivalence point:

$$[\mathrm{salt}] = [\mathrm{acid}], \text{ so } [\mathrm{salt}]/[\mathrm{acid}] = 1$$

The logarithm to the base 10 of 1 (lg 1) = 0.

So, the equation becomes:

$$\mathrm{pH} = \mathrm{p}K_a$$

ALTERNATIVE METHOD

This method has been called the 'half-volume method'.

- Using a volumetric pipette, place 25.0 cm3 of an aqueous solution of the weak acid into a conical flask.

- Add a few drops of phenolphthalein indicator.

- Titrate against a solution of aqueous sodium hydroxide until the end point colour is obtained.

- Note the volume of sodium hydroxide required. This is the minimum volume required to completely react with the acid.

- Use a fresh 25.0 cm3 sample of the same aqueous solution of the weak acid and the same aqueous solution of sodium hydroxide, but this time do not add the phenolphthalein.

- Add only half the volume of sodium hydroxide required to react with the acid.

- Measure the pH of this solution. This pH value is equal to the pK, value of the acid.