8 Acids and bases

Learning objectives

- Understand and recognise the Brønsted–Lowry definitions of acids and bases
- Recognise Brønsted–Lowry acids and bases

Figure 8.1 These all contain acids. Cola is a solution of phosphoric acid, among other things.

Acid	Formula
hydrochloric	HCl
sulfuric	H_2SO_4
nitric	HNO_3
carbonic	H_2CO_3
ethanoic	CH_3COOH
benzoic	C_6H_5COOH

Table 8.1 The formulas for some common acids, with the H that is lost as H^+ shown in red.

It was originally thought that all acids contain oxygen, and the names of this element in English, German (Sauerstoff) and other languages reflect this mistaken assumption.

Conjugate acid–base pairs always differ by one proton (H^+).

8.1 Theories of acids and bases

Acids and bases are substances that are familiar, both in the laboratory and in everyday life. A few everyday acids are shown in Figure 8.1. Examples of acids include hydrochloric acid (HCl) and sulfuric acid (H_2SO_4), and bases include sodium hydroxide (NaOH) and ammonia (NH_3).
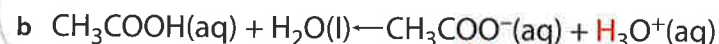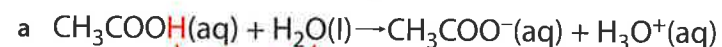
If we look at the formulas of some acids (Table 8.1), we can see that all acids contain at least one hydrogen atom. It is this hydrogen atom that leads to the characteristic properties of an acid. In the simplest definition of acids and bases, an acid is defined as a substance that produces hydrogen ions in solution, and a base is a substance that produces hydroxide ions in solution.

Brønsted–Lowry acids and bases

The **Brønsted–Lowry** definition is:
- an **acid** is a proton (H^+) **donor**
- a **base** / alkali is a proton (H^+) **acceptor**

Consider the reaction of ethanoic acid with water (Figure 8.2). In the forward direction (Figure 8.2a), the CH_3COOH donates a proton (H^+) to the H_2O – so the CH_3COOH is an acid, because it donates a proton. The H_2O accepts a proton and therefore acts as a base. In the reverse direction (Figure 8.2b), H_3O^+ donates a proton to CH_3COO^- – so H_3O^+ is an acid and CH_3COO^- is a base.

a $CH_3COOH(aq) + H_2O(l) \longrightarrow CH_3COO^-(aq) + H_3O^+(aq)$

H⁺ donated

b $CH_3COOH(aq) + H_2O(l) \longleftarrow CH_3COO^-(aq) + H_3O^+(aq)$

H⁺ donated

Figure 8.2 The reaction of ethanoic acid with water. **a** In the forward direction ethanoic acid acts as an acid because it donates a proton to water; **b** in the reverse direction, H_3O^+ acts as an acid because it donates a proton to CH_3COO^-.
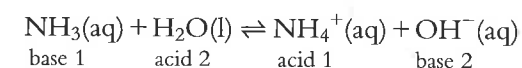
When CH_3COOH acts as an acid and donates a proton, it forms a base, CH_3COO^-. CH_3COO^- is called the **conjugate base** of CH_3COOH. CH_3COOH and CH_3COO^- are called a **conjugate acid–base pair**. Similarly, when H_2O acts as a base and accepts a proton, it forms H_3O^+, which acts as an acid in the reverse direction. H_3O^+ is the **conjugate acid** of H_2O, and H_3O^+ and H_2O are also a conjugate acid–base pair. We can label the conjugate acid–base pairs in the equation:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$
acid 1   base 2   base 1   acid 2
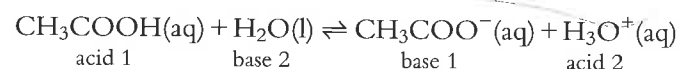
Species with the same number form a conjugate pair.

Let us look at another example:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
base 1   acid 2   acid 1   base 2

In the forward direction: H_2O donates a proton to NH_3. H_2O therefore acts as an acid and as NH_3 accepts the proton it acts as a base.

When H_2O donates the proton, it forms OH^-. OH^- is the conjugate base of H_2O, and H_2O and OH^- are a conjugate acid–base pair. We could also say that H_2O is the conjugate acid of OH^-.
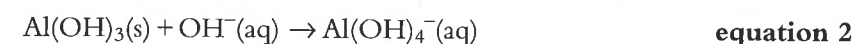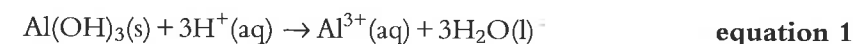
In the reverse direction: NH_4^+ donates a proton to OH^-. NH_4^+ therefore acts as an acid, and as OH^- accepts the proton, it acts as a base.

When NH_3 accepts a proton it forms NH_4^+. NH_4^+ is the conjugate acid of NH_3, and NH_3 and NH_4^+ are a conjugate acid–base pair. We could also say that NH_3 is the conjugate base of NH_4^+.

Amphiprotic and Amphoteric

These two terms are used to describe a substance can act as both an acid and a base. Amphiprotic refers to the Bronsted–Lowry definition of acids and bases and indicates a species that can donate (acting as an acid) or accept (acting as a base) a proton. Water is a substance that is amphiprotic and we have seen above that it acted as a proton donor (to form OH^-) in its reaction with NH_3 but as a proton acceptor (to form H_3O^+) in its reaction with CH_3COOH.

Amphoteric is a more general term and refers to a substance that can act as an acid and a base – all amphiprotic substances are also amphoteric but not all amphoteric substances are amphiprotic. The difference arises because there is another, more general, definition of acids and bases (the Lewis definition), which does not require the transfer of a proton. The most commonly encountered substances that are amphoteric but not amphiprotic are hydroxides of some metals such as aluminium or zinc.

$$Al(OH)_3(s) + 3H^+(aq) \rightarrow Al^{3+}(aq) + 3H_2O(l) \qquad \textbf{equation 1}$$

$$Al(OH)_3(s) + OH^-(aq) \rightarrow Al(OH)_4^-(aq) \qquad \textbf{equation 2}$$

Equation 1 shows aluminium hydroxide reacting with an acid – acting as a base and equation 2 shows it reacting with a base and therefore acting as an acid.

Nature of science

Many common acids (HNO_3, H_2SO_4 etc.) contain oxygen and in the late 18th and early 19th centuries it was thought that acids are substances that contain oxygen. However, the discovery, by Humphry Davy, that muriatic acid (hydrochloric acid) does not contain oxygen paved the way for new theories, based on hydrogen, about the nature of acids.

The hydrated proton may be written as $H^+(aq)$ or $H_3O^+(aq)$. H_3O^+ (called the hydronium ion, hydroxonium ion or oxonium ion) has the structure shown in Figure 8.3. It is essentially just an aqueous hydrogen ion (proton) and is often just written as $H^+(aq)$.
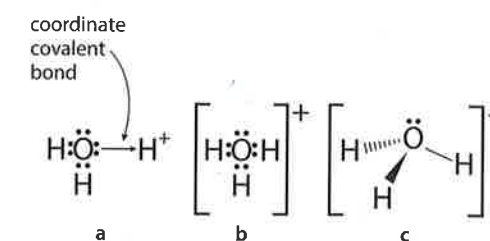
Figure 8.3 Three different representations of the structure of H_3O^+: **a** and **b** the electronic structure; **c** the trigonal pyramidal shape.

Another amphiprotic species, HCO_3^-, is discussed on page 321.

? Test yourself

1 Define acids and bases according to the Brønsted–Lowry definition.

2 Write an equation for the reaction between ammonia and ethanoic acid, classifying each species as either an acid or base and indicating the conjugate acid-base pairs.

3 Give the formula of the conjugate acid of each of the following:
   a NH_3
   b OH^-
   c HSO_4^-
   d CN^-
   e HPO_4^{2-}

4 Give the formula of the conjugate base of each of the following:
   a HCO_3^-
   b H_2O
   c $HCOOH$
   d NH_3

5 In each of the following reactions state whether the species in **bold** is acting as an acid or a base according to the Brønsted–Lowry definition:
   a $\mathbf{HSO_4^-}(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$
   b $\mathbf{HCO_3^-}(aq) + HSO_4^-(aq)$
      $\rightleftharpoons H_2CO_3(aq) + SO_4^{2-}(aq)$
   c $\mathbf{CH_3COOH}(aq) + H_2SO_4(aq)$
      $\rightleftharpoons CH_3COOH_2^+(aq) + HSO_4^-(aq)$

Learning objectives

- Understand the Lewis definition of acids and bases
- Recognise Lewis acids and bases

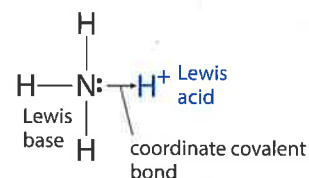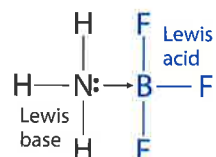**Figure 8.4** Protonation of ammonia.

Figure 8.5 An adduct is formed when NH_3 and BF_3 react together.

8.2 Lewis acids and bases (HL)

The Brønsted–Lowry definition of acids and bases is only one of several definitions of acids and bases – we will now consider the Lewis definition.

Brønsted–Lowry
- An **acid** is a proton (H^+) **donor**.
- A **base** / alkali is a proton (H^+) **acceptor**.

Lewis
- An **ACid** is an electron **pair ACceptor**.
- A **base** is an electron **pair donor**.

The Lewis definition is more general than the Brønsted–Lowry definition and can be applied to reactions that do not involve the transfer of protons. It is also useful when considering acid–base reactions in solvents other than water.

The Lewis definition of acids and bases covers all the Brønsted–Lowry reactions, because the acceptance of a proton by a base must involve the donation of an electron pair to the proton. Consider the protonation of ammonia (Figure **8.4**):

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$

NH_3 is the Lewis base, because it donates an electron pair to H^+, which is the electron pair acceptor, i.e. Lewis acid.

The reaction between BF_3 and NH_3 (Figure **8.5**) is a Lewis acid–base reaction that does not involve the transfer of a proton:

$$NH_3 + BF_3 \rightleftharpoons H_3N:BF_3$$
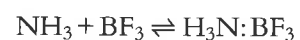
A coordinate (dative) covalent bond is always formed in a Lewis acid–base reaction.

The formation of a complex ion by a transition metal ion (Figure **8.6**) is another example of a Lewis acid–base reaction. The transition metal ion is the Lewis acid and the ligand is the Lewis base. The ligands bond to the transition metal ion through the formation of coordinate covalent bonds. For example:

$$Fe^{2+} + 6H_2O \rightleftharpoons [Fe(H_2O)_6]^{2+}$$
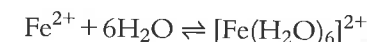
The last two reactions would not be described as acid–base reactions according to the Brønsted–Lowry theory.

For a substance to act as a Lewis base, it must have a lone pair of electrons. For a substance to act as a Lewis acid, it must have space to accept a pair of electrons in its outer shell.

For example, NH_3 and H_2O can both act as Lewis bases, because they have a lone pair of electrons – H^+ and BX_3 (where X is a halogen) can act as Lewis acids because they have space in their outer shells to accept a pair of electrons.

The Lewis definition is used sometimes to describe reactions in organic chemistry – this will be discussed in Topic **10**.

In all further discussion of the behaviour and properties of acids, we will be using the Brønsted–Lowry definition.

Figure 8.6 A transition metal complex ion.

The relationship between depth and simplicity

There are various theories of acids and bases. We have met the Brønsted–Lowry and Lewis theories. The Lewis theory is more sophisticated and extends the Brønsted–Lowry theory, which is limited to describing the acid–base behaviour of species in aqueous solution. The Lewis theory can be used to describe the acid–base reactions of substances, including those not containing hydrogen atoms, in a variety of different solvents. The Lewis theory can be applied to reactions in organic chemistry – a nucleophile is a Lewis base, and the reaction between an electrophile and a nucleophile is a Lewis acid–base reaction. The reaction of a transition metal with a ligand such as CO is a Lewis acid–base reaction. To what extent is it useful to describe these reactions as acid–base reactions? Before we knew about the Lewis theory, we probably had a fairly good picture in our minds as to what an acid–base reaction is. Have we got a more sophisticated theory at the expense of losing an understanding of what an acid–base reaction is?
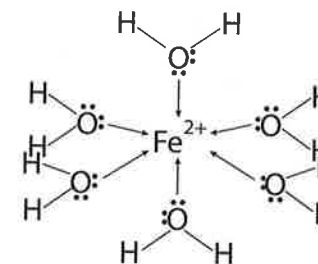
? Test yourself

6 Define acids and bases according to the Lewis definition.

7 Classify each of the following as a substance that can act as a Lewis acid or as a Lewis base:
   H_2O BF_3 HCO_3^- H^+ $AlCl_3$ NH_3 CO

Learning objectives

- Describe the reactions of acids with metals, bases, alkalis, carbonates and hydrogencarbonates

8.3 Properties of acids and bases

Salts

The hydrogen ion (H^+) in an acid can be regarded as 'replaceable' and can be replaced by a metal ion (or ammonium ion) to form a **salt**. For example, if the hydrogen ions in sulfuric acid are replaced by sodium ions, the salt called sodium sulfate (Na_2SO_4) is formed. The names of the salts formed by some acids are given in Table **8.2**.

Acid	Formula	Name of salt	Example of salt
hydrochloric	**H**Cl	chloride	NaCl
sulfuric	**H**$_2$SO$_4$	sulfate	Na$_2$SO$_4$
nitric	**H**NO$_3$	nitrate	NH$_4$NO$_3$
carbonic	**H**$_2$CO$_3$	carbonate	K$_2$CO$_3$
ethanoic	CH$_3$COO**H**	ethanoate	Ca(CH$_3$COO)$_2$

Table 8.2 The formulas for some common acids and their salts – a hydrogen lost as H^+ is shown **bold**.
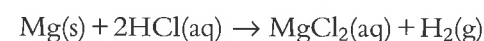
The reactions of acids and bases

The characteristic reactions of acids are described below. In each case we can write an ionic equation where the acid is represented by $H^+(aq)$.

Reactions of acids with metals

The general equation for these reactions is:

metal + acid → salt + hydrogen

Acids react with reactive metals such as magnesium to produce a salt and hydrogen gas. For example:

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

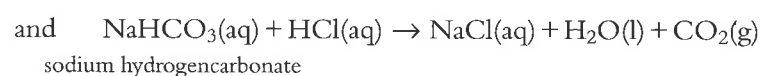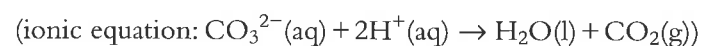Ionic equation: $Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$

Unreactive metals such as copper do not react with dilute acids.

Reactions of acids with carbonates and hydrogencarbonates

acid + carbonate / hydrogencarbonate → salt + carbon dioxide + water

For example:

$$Na_2CO_3(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + H_2O(l) + CO_2(g)$$

(ionic equation: $CO_3^{2-}(aq) + 2H^+(aq) \rightarrow H_2O(l) + CO_2(g)$)

and $NaHCO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l) + CO_2(g)$
sodium hydrogencarbonate

The reactions of nitric acid with metals tend to be different from that given here and other products are obtained.

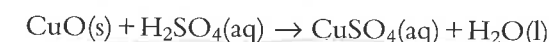Metals lower than hydrogen in the activity series (Topic **9**) will not react with acids.

Reactions of acids with bases and alkalis

Bases are metal oxides or metal hydroxides, such as copper(II) oxide or calcium hydroxide. These react with acids to form a salt and water.
For example:

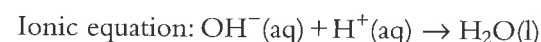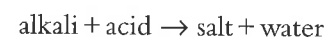$$CuO(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + H_2O(l)$$

Alkalis are solutions obtained when a metal hydroxide (such as sodium hydroxide) dissolves in water or when certain bases react with water. For instance, the base sodium oxide (Na_2O) reacts with water to produce the alkali sodium hydroxide:

$$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$$
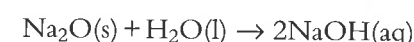
There are very few soluble metal hydroxides and so there are very few alkalis. The most common alkalis are the alkali metal hydroxides (e.g. sodium hydroxide solution), ammonia solution and barium hydroxide solution.

The terms 'alkali' and 'base' are often used interchangeably. 'Base' is the more general term and will be used in all of the discussions in subsequent sections.

The reaction between an acid and an alkali is similar to that between an acid and a base:

alkali + acid → salt + water

For example: $NaOH(aq) + HNO_3(aq) \rightarrow NaNO_3(aq) + H_2O(l)$

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

The reactions between acids and bases or acids and alkalis are called **neutralisation** reactions and essentially just involve the H^+ ions from the acid reacting with the OH^- ions from the alkali to form the neutral substance water. Neutralisation reactions are exothermic and typically give out about 57 kJ per mole of water formed.

The reactions of acids with ammonia solution, an alkali, are often written slightly differently:

$$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$$
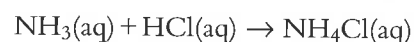
Ammonia solution is equivalent to ammonium hydroxide (NH_4OH) – in some laboratories bottles are labelled 'ammonia solution' and in others they are labelled 'ammonium hydroxide'. Ammonia is in equilibrium with the ammonium ion and the hydroxide ion:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
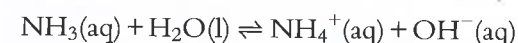
The reaction with hydrochloric acid could also have been written:

$$NH_4OH(aq) + HCl(aq) \rightarrow NH_4Cl(aq) + H_2O(l)$$
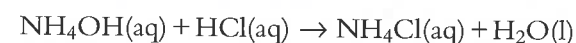
which corresponds to the general equation of alkali + acid → salt + water.

base + acid → salt + water

Neutralisation reactions are exothermic and produce a salt and water only.
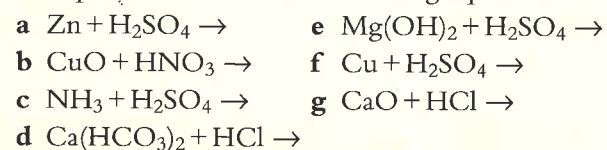
Making salts from acids and bases

Generally the metal part of the salt comes from a metal oxide or hydroxide and the non-metal part from the acid. So, copper sulfate can be made from the reaction between the base copper oxide and sulfuric acid. Sodium nitrate can be made from the base sodium oxide (or the alkali sodium hydroxide) and nitric acid.

One common way of making a soluble salt is by titrating an acid against an alkali. A known amount of acid is measured out using a pipette and then an indicator is added. The alkali is then added from a burette until the indicator just changes colour. The experiment is then repeated using the same amounts of acid and alkali but without the indicator. The titration technique is covered on page **43**.

Indicators are essentially substances that have different colours in acidic and alkaline solutions – for example, bromothymol blue is yellow in acidic solution and blue in alkaline solution. Many different indicators can be used for titrations and they are chosen according to whether the acid or the alkali is strong or weak (see page **349**). Universal indicator contains a mixture of indicators and cannot be used to monitor titrations because it changes gradually from one colour to the next.

? Test yourself

8 Complete and balance the following equations:
 a $Zn + H_2SO_4 \rightarrow$ **e** $Mg(OH)_2 + H_2SO_4 \rightarrow$
 b $CuO + HNO_3 \rightarrow$ **f** $Cu + H_2SO_4 \rightarrow$
 c $NH_3 + H_2SO_4 \rightarrow$ **g** $CaO + HCl \rightarrow$
 d $Ca(HCO_3)_2 + HCl \rightarrow$

9 State the name of an acid and a base that would react together to form each of these salts:
 a calcium nitrate
 b cobalt(II) sulfate
 c copper(II) chloride
 d magnesium ethanoate

Learning objectives

- Use pH values to distinguish between acidic, neutral and alkaline solutions
- Understand that pH provides a measure of the concentration of H^+ ions in aqueous solution
- Solve problems involving pH
- Write an equation for the dissociation of water and state the expression for K_w
- Use K_w values to work out the concentrations of $H^+(aq)$ and $OH^-(aq)$ and the pH of aqueous solutions

8.4 The pH scale

Measuring pH

The pH scale can be used to indicate whether a solution is acidic, alkaline or neutral. At 25 °C, a solution with pH lower than 7 is acidic, a solution with pH 7 is neutral and a solution with pH greater than 7 is alkaline (Figure **8.7**).

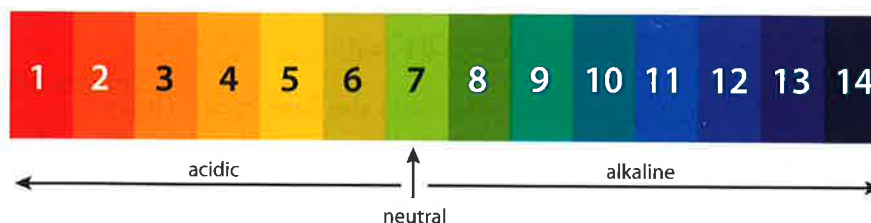acidic   neutral   alkaline

Figure 8.7 The pH scale showing the colours of universal indicator.

The pH of a solution can be determined by using a **pH meter** or by using universal indicator solution or paper.

pH is a measure of the concentration of $H^+(aq)$ ions in a solution. The concentration of H^+ ions can be stated in $mol\,dm^{-3}$, but the use of the log_{10} function simplifies the numbers involved.

> **Definition: pH is the negative logarithm to base 10 of the hydrogen ion concentration in an aqueous solution.**
>
> $$pH = -log_{10}[H^+(aq)]$$

So, if the concentration of H^+ ions in a solution is $1.57 \times 10^{-3}\,mol\,dm^{-3}$, the pH is worked out as:

$$pH = -log_{10}(1.57 \times 10^{-3}) = 2.80$$

pH has no units.

> Because pH is a log scale (to base 10), a 1 unit change in pH indicates a tenfold change in the H^+ ion concentration (see Table **8.3**).

Note: the '10' is often omitted in 'log_{10}', giving $pH = -log[H^+(aq)]$. To work out pH, use the 'log' button on a calculator.

$[H^+(aq)]/mol\,dm^{-3}$	pH
1	0
0.1	1
0.01	2
1×10^{-3}	3
1×10^{-4}	4
1×10^{-5}	5
1×10^{-6}	6
1×10^{-7}	7
1×10^{-8}	8

Table 8.3 pH values and the corresponding concentration of H^+ ions.

The pH for solutions in which the concentration of H^+ ions is a power of 10 can be worked out without using a calculator by understanding how the log_{10} function works.

$$log_{10}\,100 = 2 \qquad\qquad 10^2 = 100$$

$$log_{10}\,100 = 2$$

The log of a number is the power that 10 must be raised to in order to equal that number.

0.01 can be written as a power of **10**: $0.01 = 10^{-2}$

so $log_{10}\,0.01 = -2$

$$log_{10}\,0.01 = -2$$

Therefore, if a solution has an $H^+(aq)$ concentration of $0.01\,mol\,dm^{-3}$, the pH of this solution is given by:

$$pH = -log_{10}\,0.01 = 2$$

Note: the power that 10 must be raised in order to equal 1 is 0; therefore $log_{10}\,1 = 0$.

Calculating [H⁺(aq)] from a pH

To calculate $[H^+(aq)]$ from a pH, the inverse function of log_{10} must be used. So 10 must be raised to the power of $-pH$.

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

This is usually done using the '2nd' (or 'shift') and 'log' key combination on a calculator.

The dissociation of water

Water dissociates (or ionises) according to the equation:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$
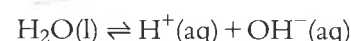
The degree of dissociation is very small and, at 25 °C, in pure water the concentrations of H^+ and OH^- ions are equal at $1.0 \times 10^{-7}\,mol\,dm^{-3}$.

An equilibrium constant, K_w, can be written for this reaction:

$K_w = [H^+(aq)][OH^-(aq)]$
K_w is called the **ionic product constant** (ionic product) for water.
K_w has a value of 1.0×10^{-14} at 298 K.

K_w refers to the $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ equilibrium in all aqueous solutions – the product of the H^+ and OH^- concentrations in **any** aqueous solution at 298 K is 1.0×10^{-14}.

The concentration of water is not incorporated in the equilibrium expression because water is in excess and its concentration is essentially constant.
Also note that K_w has no units because the concentrations that we are using are compared to a standard concentration of $1\,mol\,dm^{-3}$. When we write $[H^+(aq)]$ here, what we actually mean is 'the concentration of H^+ ions divided by $mol\,dm^{-3}$', which has no units – therefore K_w has no units. For advanced work, K_w should be worked out in terms of activities (effective concentrations), which are also compared to a standard concentration.

Consider a $0.10\,mol\,dm^{-3}$ solution of hydrochloric acid. HCl is a strong acid and dissociates completely in solution – therefore the concentration of H^+ ions in solution will be $0.10\,mol\,dm^{-3}$. Now, $[H^+(aq)][OH^-(aq)] = 1.0 \times 10^{-14}$ so the concentration of OH^- ions in this solution must be $1.0 \times 10^{-13}\,mol\,dm^{-3}$ because $0.10 \times (1 \times 10^{-13}) = 1.0 \times 10^{-14}$. So, even a solution of an acid contains some OH^- ions because of the ionisation of water.

Similarly, the concentration of H^+ ions in a $1.0 \times 10^{-3}\,mol\,dm^{-3}$ solution of sodium hydroxide (a strong base) is $1.0 \times 10^{-11}\,mol\,dm^{-3}$. The presence of H^+ ions from the ionisation of water in all aqueous solutions explains why we can always measure a pH.

We can understand whether solutions are acidic, alkaline or neutral in terms of the relative concentrations of H^+ and OH^-.

A solution is:
• neutral if $[H^+(aq)] = [OH^-(aq)]$
• acidic if $[H^+(aq)] > [OH^-(aq)]$
• alkaline if $[OH^-(aq)] > [H^+(aq)]$

Calculating pH values

For now, we will limit the calculation of pH to solutions of strong acids and bases – calculations involving weak acids and bases will be covered in Subtopic **8.7**.

Calculating the pH of a solution of a strong acid

Because strong acids can be assumed to dissociate fully in aqueous solution (see Subtopic **8.5**), the concentration of H^+ ions is the same as the concentration of the acid.

Example

We shall calculate the pH of a $0.001\,50\,mol\,dm^{-3}$ solution of hydrochloric acid. The acid is strong, so full dissociation produces an $H^+(aq)$ concentration of $0.001\,50\,mol\,dm^{-3}$ (the same as the original acid):

$$pH = -\log_{10}[H^+(aq)] = -\log_{10}[0.001\,50] = 2.82$$

Worked example

8.1 **a** What is the pH of $10\,cm^3$ of $0.10\,mol\,dm^{-3}$ hydrochloric acid?

   b If $90\,cm^3$ of water is added to the acid, what happens to the pH?

   c If the solution from part **b** is now diluted by a factor of a million (10^6), what is the approximate pH of the final solution?

a HCl is a strong acid and dissociates fully, so the concentration of $H^+(aq)$ is $0.10\,mol\,dm^{-3}$ and

$$pH = -\log_{10}[H^+(aq)] = -\log_{10}[0.10] = 1.0$$

b If $90\,cm^3$ of water is added to $10\,cm^3$ of acid, the total volume of the solution becomes $100\,cm^3$. There are the same number of H^+ ions in 10 times the volume – the concentration of H^+ ions has been reduced by a factor of 10. Because pH is a log scale, a reduction in $[H^+(aq)]$ by a factor of 10 results in the pH of the solution increasing by 1. So the pH of the diluted solution is 2.0.

We can also consider this in terms of numbers. The initial concentration of $H^+(aq)$ is $0.10\,mol\,dm^{-3}$. When this is diluted by a factor of 10, the concentration of $H^+(aq)$ decreases to $0.010\,mol\,dm^{-3}$.

$$pH = -\log_{10}[H^+(aq)] = -\log_{10}[0.010] = 2.0$$

c Diluting a solution by a factor of 10 causes the pH to increase by 1 unit, so it might be expected that diluting the solution in part **b** by a factor of 10^6 would cause its pH to increase by 6 units to 8.0. However, it is not possible to dilute an acidic solution so that it becomes an alkaline solution; we have ignored the dissociation of water molecules into H^+ and OH^- ions. The actual pH of this solution will be slightly less than 7. If the solution is diluted further, the pH will get closer and closer to 7, but never reach it.

Calculating the pH of a solution of a strong base

The pH of an alkaline solution can be worked out using the ionic product constant, K_w, equal to 1.00×10^{-14} at 25 °C.

Worked example

8.2 Calculate the pH of a $0.250\,mol\,dm^{-3}$ solution of potassium hydroxide at 25 °C.

$$KOH(aq) \rightarrow K^+(aq) + OH^-(aq)$$
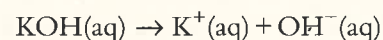
KOH is a strong base, so, the OH^- concentration is the same as that of the original base – i.e. $0.250\,mol\,dm^{-3}$.

> Strong bases are completely ionised in solution.

Now, $K_w = [H^+(aq)][OH^-(aq)]$ and, at 25 °C, $K_w = 1.00 \times 10^{-14}$.

Substituting the OH^- concentration and the value of K_w into this expression we obtain:

$$1.00 \times 10^{-14} = [H^+(aq)] \times 0.250$$

So $[H^+(aq)] = 4.00 \times 10^{-14}\,mol\,dm^{-3}$

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

$$= -\log_{10}(4.00 \times 10^{-14})$$

$$= 13.4$$

Nature of science

It is important that scientists are able to communicate their findings and discuss issues with non-scientists. pH is an example of a concept that allows discussion of acidity without the requirement for a complete understanding of the theory – stating that the pH of acid rain is 4 is much simpler than saying that the concentration of hydrogen ions is $1 \times 10^{-4}\,mol\,dm^{-3}$.

? Test yourself

10 Arrange the following in order of increasing pH:
  - $0.010\,mol\,dm^{-3}$ HCl
  - $1.0\,mol\,dm^{-3}$ NaOH
  - $0.10\,mol\,dm^{-3}$ H_2SO_4
  - $0.10\,mol\,dm^{-3}$ HCl

11 State whether each of the following statements is **true** or **false**:
  - **a** The pH of $0.10\,mol\,dm^{-3}$ HCl is 2.
  - **b** The $[H^+]$ in a solution of pH = 3 is 100 times the $[H^+]$ in a solution of pH = 5.
  - **c** The $[H^+]$ in a solution of pH = 13 is $1.0 \times 10^{13}\,mol\,dm^{-3}$.
  - **d** The pH of $0.010\,mol\,dm^{-3}$ H_2SO_4 is 2.

12 A solution of $0.2\,mol\,dm^{-3}$ HCl has a pH of 0.7. Of this solution, $25.0\,cm^3$ is taken and made up to a total volume of $250\,cm^3$ with distilled water in a volumetric flask to form solution **X**. $10.0\,cm^3$ of solution **X** is taken and made up to a total volume of $1.00\,dm^3$ with distilled water in a volumetric flask; this is solution **Y**.
  - **a** Work out the pH value for each solution.
  - **b** Suggest an experimental method, other than measuring the pH or using universal indicator, that could be used to distinguish between solution **X** and solution **Y**.

13 Copy and complete the following table by working out pH values. The first three should be done without using a calculator.

a solution containing $0.001\,00\,mol\,dm^{-3}$ $H^+(aq)$	
a solution containing $1.00 \times 10^{-12}\,mol\,dm^{-3}$ $H^+(aq)$	
a solution of $1.00\,mol\,dm^{-3}$ HCl(aq)	
a solution of $2.00 \times 10^{-4}\,mol\,dm^{-3}$ HNO_3(aq)	
a solution of CH_3COOH of concentration $0.100\,mol\,dm^{-3}$ assuming 5% dissociation of the acid	

14 Calculate the concentration of H^+ ions in each of the following solutions:
  - **a** pH = 3.5
  - **b** pH = 7.9
  - **c** pH = 12.8

15 Copy and complete the table for aqueous solutions at 25 °C – try to do it without using a calculator. The first row has been completed for you.

| $[H^+(aq)]/$ $mol\,dm^{-3}$	$[OH^-$ $(aq)]/$ $mol\,dm^{-3}$	pH	Acidic or alkaline?
1.0×10^{-3}	1.0×10^{-11}	3	acidic
1.0×10^{-5}	1×10^{-9}	5	acidic
1×10^{-12}	0.01	12	Alkali

16 Calculate the pH of these aqueous solutions assuming that both species ionise completely:
  - **a** $0.0150\,mol\,dm^{-3}$ NaOH
  - **b** $0.0500\,mol\,dm^{-3}$ $Ba(OH)_2$

17 Calculate the concentration of OH^- ions in:
  - **a** $0.020\,mol\,dm^{-3}$ HCl(aq)
  - **b** $1.4 \times 10^{-4}\,mol\,dm^{-3}$ HNO_3(aq)

8.5 Strong and weak acids and bases

Acids

When an acid (HA) reacts with water it **dissociates**, or **ionises**:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$
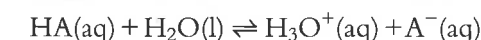
This can be understood using the Brønsted–Lowry theory – the acid donates a proton to water. Basically, though, what has happened is that the acid has dissociated into H^+ and A^- ions. This reaction is, therefore, often simplified to:

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

This reaction is exactly the same as the one above, and the H^+ from the acid is still donated to H_2O, but the 'H_2O' has been omitted for simplicity ($H^+(aq)$ is equivalent to $H_3O^+(aq)$).

We can classify acids as strong or weak according to how much they dissociate in aqueous solution.

Learning objectives

- Understand the difference between strong and weak acids and bases
- Recognise examples of strong and weak acids and bases
- Describe and explain experiments to distinguish between strong and weak acids and bases

Strong acids

Strong acids such as hydrochloric (HCl), sulfuric (H_2SO_4) and nitric (HNO_3) acid dissociate completely in aqueous solution (see Figure 8.8).
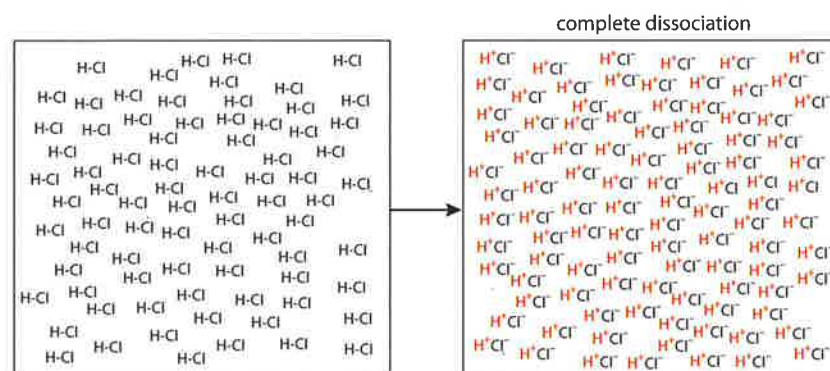

Figure 8.8 HCl dissociates completely in aqueous solution.

This can be represented as:

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

The non-reversible arrow ($\rightarrow$) is used to indicate that dissociation is essentially complete.

HCl is a **monoprotic acid** – it dissociates to form one proton per molecule. H_2SO_4 is a **diprotic acid** – it can dissociate to form two protons per molecule:

$$H_2SO_4(aq) + H_2O(l) \rightarrow HSO_4^-(aq) + H_3O^+(aq)$$

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$$
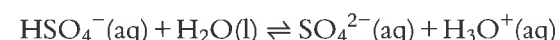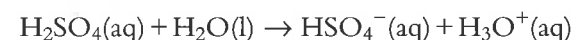
Sulfuric acid is a strong acid for the first dissociation only.

Weak acids

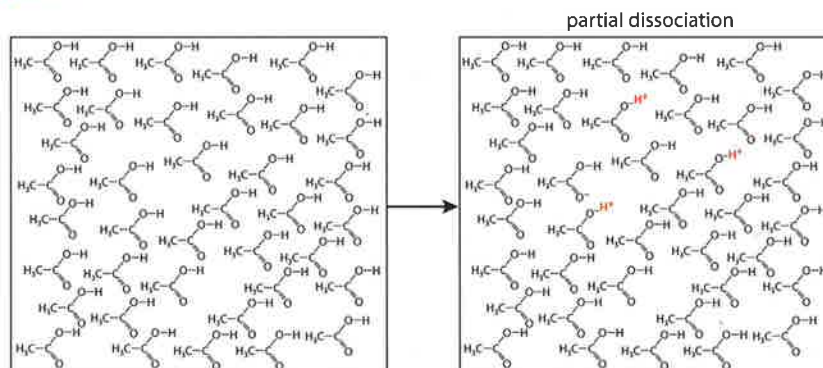**Weak acids dissociate only partially in aqueous solution (see Figure 8.9).**

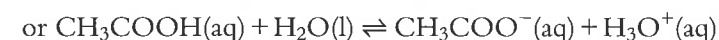**Figure 8.9** Only a few of the ethanoic acid molecules dissociate.

Examples of weak acids are carbonic acid (H_2CO_3) and carboxylic acids such as ethanoic acid (CH_3COOH).

The dissociation of a weak acid is represented by:

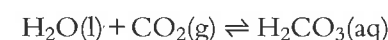$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

The equilibrium arrow is essential and indicates that the reaction is reversible and does not go to completion.

The dissociation of ethanoic acid is represented by:

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

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

Carbonic acid is formed when carbon dioxide dissolves in water (see Figure 8.10):

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

It is a diprotic acid and its dissociation can be shown as:

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

$$HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H^+(aq)$$

Many scientists believe that increasing levels of CO_2 in the atmosphere resulting from human activity, such as the burning of fossil fuels, are making the oceans more acidic as more CO_2 dissolves in them. Some scientists believe that the pH of the oceans could drop by up to 0.5 units by the end of the century and this could have a disastrous effect on coral reefs because these are limestone ($CaCO_3$) structures.
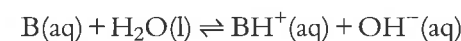

Figure 8.10 Carbonated water is acidic because of dissolved CO_2.

HCO_3^-, the hydrogencarbonate ion, is amphiprotic. It accepts a proton in the reverse reaction in the first equation (acts as a base) and donates a proton (acts as an acid) in the second.

Bases

When a base (B) reacts with water, it accepts a proton from the water and ionises according to:

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

Bases are defined as strong or weak depending on how much they ionise in aqueous solution.

Strong bases

Strong bases ionise completely in aqueous solution.

For example, sodium hydroxide ionises completely to produce OH^- ions:

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

Strong bases include the group 1 hydroxides (LiOH, NaOH etc.) and Ba(OH)$_2$.

Exam tip
Ba(OH)$_2$ ionises in aqueous solution to give $2OH^-$:

$$Ba(OH)_2(aq) \rightarrow Ba^{2+}(aq) + 2OH^-(aq)$$
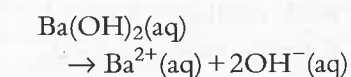
So $1\,mol\,dm^{-3}$ Ba(OH)$_2$(aq) contains $2\,mol\,dm^{-3}$ OH^-.

Weak bases

| **Weak bases ionise only partially in aqueous solution.**

Ammonia is a typical weak base and ionises according to the equation:

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

In a $0.10\,mol\,dm^{-3}$ solution of ammonia (at $25\,°C$) about 1.3% of the molecules are ionised.

Other weak bases are amines such as ethylamine (ethanamine), $CH_3CH_2NH_2$. Ethylamine ionises according to the equation:

$$CH_3CH_2NH_2(aq) + H_2O(l) \rightleftharpoons CH_3CH_2NH_3^+(aq) + OH^-(aq)$$

At $25\,°C$, a $0.10\,mol\,dm^{-3}$ solution of ethylamine has about 7.1% of the molecules ionised – so ethylamine is a stronger base than ammonia.
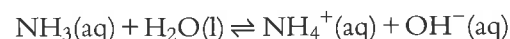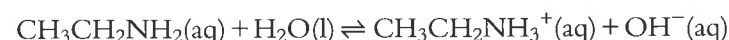
## The relationship between the strength of an acid and the strength of its conjugate base

| **The stronger an acid, the weaker its conjugate base.**

A strong acid such as HCl dissociates completely in aqueous solution:

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

The conjugate base of HCl is Cl^- – this is a very weak base because it has virtually no tendency to react with H_2O or H^+ to re-form HCl – the above reaction goes essentially to completion.

HCN, on the other hand, is a very weak acid and has very little tendency to dissociate:

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$$
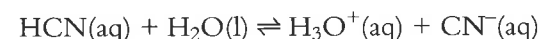
The position of equilibrium lies a long way to the left – CN^- has a strong tendency to pick up H^+ from H_3O^+, that is, to act as a base.

The conjugate base of HCN is a much stronger base than that of HCl (Cl^-) and when it is added to water it reacts to re-form the parent acid:

$$CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$$
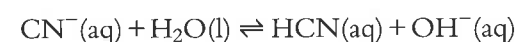
| **The stronger a base, the weaker its conjugate acid.**

A weak base ionises partially in aqueous solution:

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$
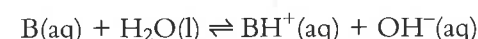
The stronger the base, the further the position of this equilibrium lies to the right and the less tendency the conjugate acid (BH^+) has to donate a proton to re-form B.

- A strong acid is a good proton donor that ionises completely in aqueous solution – it has a weak conjugate base.
- A strong base is a good proton acceptor that ionises completely in aqueous solution – it has a weak conjugate acid.

So, ethylamine (stronger base) has a weaker conjugate acid than ammonia (weaker base).

Distinguishing between strong and weak acids and between strong and weak bases

The methods for distinguishing between acids rely on the fact that strong acids dissociate more than weak acids.

In the following examples we will compare solutions of strong and weak acids of **equal concentrations**. When comparing strong and weak acids, it is essential that the solutions have the same concentration because the total concentration of H^+ ions in a concentrated solution of a weak acid could be higher than in a dilute solution of a strong acid.

Solutions of strong acids conduct electricity better than solutions of weak acids

A strong acid dissociates fully, so the concentration of ions is high and the solution is a good conductor of electricity. A weak acid dissociates only partially and so the concentration of ions is lower and the solution does not conduct electricity as well.

The conductivity of solutions can be measured using a conductivity meter or by looking at the brightness of a bulb in the experimental set-up shown in Figure 8.11.

Strong acids may be described as **strong electrolytes**, whereas weak acids are **weak electrolytes**. This also applies to strong and weak bases – strong bases conduct electricity better than weak bases.

Figure 8.11 The bulb glows more brightly with a solution of a strong acid than it does with a solution of weak acid.

Strong acids have a lower pH than weak acids

pH is a measure of the concentration of H^+ ions in solution – the lower the pH, the higher the concentration of H^+ ions. Strong acids dissociate more, producing a higher concentration of H^+ ions in solution (a lower pH). This can be tested using universal indicator or a pH meter. Again, this method could also be used for distinguishing between strong and weak bases. Strong bases have a higher pH than weak bases of the same concentration.

Strong acids react more violently with metals or carbonates

Strong acids have a higher concentration of free H^+ ions and therefore react more rapidly with a metal such as magnesium to form hydrogen – this can be shown by more rapid bubbling (effervescence) when the metal is added (see Figure 8.12). A similar effect is seen when a carbonate/hydrogencarbonate is added to an acid. Stronger acids would also have a faster rate of reaction with metal oxide/hydroxides, but this is harder to observe experimentally.

Figure 8.12 Magnesium reacting with a strong acid (hydrochloric acid, left) and a weak acid (ethanoic acid, right). The more violent reaction with the strong acid causes larger hydrogen bubbles, which keeps the magnesium at the surface of the fluid. The much smaller bubbles caused by the weaker acid reaction spread through the acid, making it appear milky.

Strength versus concentration

You should be aware of the difference between the concentration of an acid (or base) and its strength. The *concentration* of an acid refers to the number of moles of acid in a certain volume – e.g. in a solution of ethanoic acid of concentration $0.100\,\text{mol}\,\text{dm}^{-3}$ the total number of moles of ethanoic acid before dissociation is $0.100\,\text{mol}$ in every cubic decimetre (litre). The *strength* of an acid refers to how much it dissociates in aqueous solution.

A solution of ethanoic acid of concentration $1.00\,\text{mol}\,\text{dm}^{-3}$ is a more concentrated solution than $0.100\,\text{mol}\,\text{dm}^{-3}$ ethanoic acid. No matter how concentrated the solution of ethanoic acid is, it will never become a strong acid because it always dissociates partially. Similarly, diluting a strong acid such as hydrochloric acid does not make it anything other than a strong acid because it always dissociates fully.

pH is not a measure of acid or base strength

pH is simply a measure of the concentration of $H^+(aq)$ ions. It is possible for a dilute solution of a strong acid to have a higher pH than a concentrated solution of a weak acid. $1.00\,\text{mol}\,\text{dm}^{-3}$ ethanoic acid has a pH of 2.38, but $1.00 \times 10^{-3}\,\text{mol}\,\text{dm}^{-3}$ hydrochloric acid has a pH of 3.00. Because the solution of ethanoic acid is much more concentrated, the partial dissociation of the weak acid produces a higher concentration of $H^+(aq)$ than the complete dissociation of the strong acid HCl.

Nature of science

Advances in technology and instrumentation have allowed for the generation of quantitative data about the relative strengths of acids and bases. This has allowed scientists to look for patterns and anomalies and allowed for development of new theories at the molecular level. For instance the relative basic strengths of NH_3, H_2NCH_3 and $HN(CH_3)_2$ can be explained in terms of the electron–releasing effect of alkyl groups but the fact that $N(CH_3)_3$ is a weaker base than $HN(CH_3)_2$ required modification of the theory and an alternative explanation.

? Test yourself

18 Classify the following as strong acid, weak acid, strong base, weak base or salt:

HCl	H_2SO_4	NH_4NO_3	NaOH
NH_3	HNO_3	Na_2SO_4	H_2CO_3
$Ba(OH)_2$	KNO_3	CH_3NH_2	HCOOH

19 A solution of $0.000\,100\,\text{mol}\,\text{dm}^{-3}$ hydrochloric acid has a pH of 4.00, whereas a solution of $0.100\,\text{mol}\,\text{dm}^{-3}$ ethanoic acid has a pH of 2.88. Explain what these values tell you about the usefulness of pH as a measure of acid strength.

20 For each pair of solutions, state which will have the higher electrical conductivity:

a $0.10\,\text{mol}\,\text{dm}^{-3}$ HCOOH and $0.10\,\text{mol}\,\text{dm}^{-3}$ HCl

b $0.10\,\text{mol}\,\text{dm}^{-3}$ NH_3 and $0.10\,\text{mol}\,\text{dm}^{-3}$ KOH

c $0.10\,\text{mol}\,\text{dm}^{-3}$ HCl and $0.10\,\text{mol}\,\text{dm}^{-3}$ H_2SO_4

d $0.10\,\text{mol}\,\text{dm}^{-3}$ HNO_3 and $0.010\,\text{mol}\,\text{dm}^{-3}$ HCl
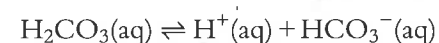
8.6 Acid deposition

Oxides of non-metals are acidic and, if soluble in water, dissolve to produce acidic solutions.

Rain is naturally acidic because of dissolved carbon dioxide:

$$H_2O(l) + CO_2(g) \rightleftharpoons H_2CO_3(aq)$$
$$\text{carbonic acid}$$
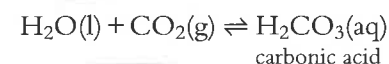
H_2CO_3 is a weak acid and dissociates partially according to the equation:

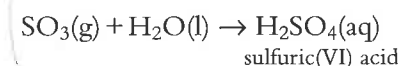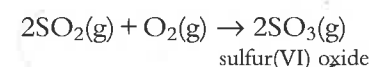$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

Because of this reaction, the pH of rain water is about 5.6. This is a natural phenomenon – rain with a pH between 5.6 and 7 is not considered to be 'acid rain'. Acid rain is considered to be rain with a pH lower than 5.6. The average pH of rain in some areas can be as low as 4.

Acidic pollutants include the oxides of sulfur and nitrogen. Sulfur dioxide (sulfur(IV) oxide) can be formed by various natural and anthropogenic processes – such as the burning of sulfur–containing fuels:

$$S(s) + O_2(g) \rightarrow SO_2(g)$$
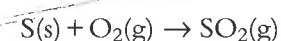
The process by which SO_2 is converted into SO_3 and H_2SO_4 in the atmosphere is complex and does not involve simple oxidation by atmospheric oxygen – interactions with hydroxyl radicals, ozone or hydrogen peroxide are involved. However, the reactions can be summarised:

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$
$$\text{sulfur(VI) oxide}$$

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$
$$\text{sulfuric(VI) acid}$$

SO_2 can also dissolve in water to produce sulfuric(IV) acid (sulfurous acid):

$$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$$
$$\text{sulfuric(IV) acid}$$
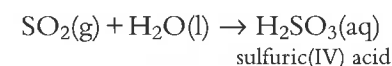
The main anthropogenic sources of nitrogen oxides are the internal combustion engine, coal, gas, oil–fuelled power stations and heavy industry power generation. The combustion temperatures of fuels in these processes are very high and oxidation of atmospheric nitrogen occurs forming NO (nitrogen monoxide, nitric oxide or nitrogen(II) oxide):

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$
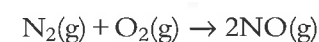
NO can be oxidised in the atmosphere to NO_2. Again, the exact nature of the process is complex but the reaction can be summarised as:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$
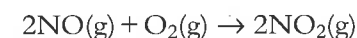
Learning objectives

- Understand what is meant by acid deposition and what causes it
- Understand some of the problems associated with acid deposition
- Understand the difference between pre- and post-combustion methods of reducing sulfur dioxide emissions

Acid deposition is a more general term than **acid rain**. It refers to any process in which acidic substances (particles, gases and precipitation) leave the atmosphere to be deposited on the surface of the Earth. It can be divided into **wet deposition** (acid rain, fog and snow) and **dry deposition** (acidic gases and particles).

'Anthropogenic' means produced by human activities.

The NO_2 can then react with a hydroxyl free radical (HO•) to form nitric(V) acid:

$$NO_2(g) + HO\bullet(g) \rightarrow HNO_3(g)$$

Other reactions can occur and the formation of nitric acid can also be shown as:
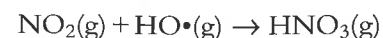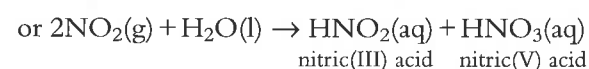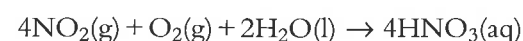
$$4NO_2(g) + O_2(g) + 2H_2O(l) \rightarrow 4HNO_3(aq)$$

or $2NO_2(g) + H_2O(l) \rightarrow \underset{\text{nitric(III) acid}}{HNO_2(aq)} + \underset{\text{nitric(V) acid}}{HNO_3(aq)}$
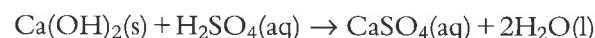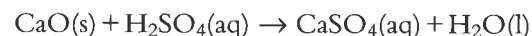
Problems associated with acid deposition

- **Effect on vegetation** – it is not necessarily the acid itself that causes problems. The acid (H^+ ions) can displace metal ions from the soil that are consequently washed away (particularly calcium, magnesium and potassium ions). Mg^{2+} ions are needed to produce chlorophyll, so plants could be prevented from photosynthesising properly. The acid rain also causes aluminium ions to dissolve from rocks, which damages plant roots and limits water uptake. This can cause stunted growth and thinning or yellowing of leaves on trees (Figure **8.13a**).
- **Lakes and rivers** – aquatic life is sensitive to the pH falling below 6. Insect larvae, fish and invertebrates, among others, cannot survive below pH 5.2. Below pH 4.0 virtually no life will survive. Acid rain can dissolve hazardous minerals from rocks, which can accumulate in lakes and damage aquatic life – in particular, Al^{3+} ions damage fish gills.
- **Buildings** – limestone and marble are eroded by acid rain and dissolve away exposing a fresh surface to react with more acid (Figure **8.13b**). A typical reaction is:

  $$CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + H_2O(l) + CO_2(g)$$

- **Human health** – acids irritate mucous membranes and cause respiratory illnesses such as asthma and bronchitis. Acidic water can dissolve heavy metal compounds releasing poisonous ions such as Cu^{2+}, Pb^{2+} and Al^{3+} which may be linked to Alzheimer's disease.

Methods of dealing with acid deposition

Methods include:
- improving the design of vehicle engines
- using catalytic converters
- removing sulfur before burning fuels
- using renewable power supplies
- making greater use of public transport
- designing more efficient power stations
- 'liming' of lakes – calcium oxide or hydroxide neutralises acidity:

  $$CaO(s) + H_2SO_4(aq) \rightarrow CaSO_4(aq) + H_2O(l)$$

  $$Ca(OH)_2(s) + H_2SO_4(aq) \rightarrow CaSO_4(aq) + 2H_2O(l)$$

Figure 8.13 Acid deposition can **a** kill trees and fish in lakes and **b** react with limestone buildings to cause erosion.

Pre- and post-combustion methods of reducing sulfur dioxide emissions

Sulfur is present in fossil fuels such as coal and various fuels obtained from crude oil, such as gasoline (petrol). When such fuels are burnt sulfur dioxide is produced, which can contribute to acid rain. To produce a more environmentally-friendly fuel the sulfur can either be removed before the fuel is burnt (pre-combustion desulfurisation) or the SO_2 can be removed after the fuel has been burnt (post-combustion desulfurisation).

The regulations governing how much sulfur can be present in gasoline and diesel are quite strict and so sulfur is removed from these fuels before they are burnt. For instance, hydrodesulfurisation (hydrotreating) can be used – this involves heating crude oil fractions with hydrogen in the presence of a catalyst. This converts the sulfur to hydrogen sulfide (H_2S), which can be removed from the reaction mixture by bubbling it through an alkaline solution. The H_2S can be subsequently converted back into sulfur and sold to other companies to make sulfuric acid.

Post-combustion methods are commonly used in coal-fired power stations and involve passing the exhaust gases from the furnace through a vessel where the sulfur dioxide can react with alkalis/bases such as calcium oxide, calcium carbonate or calcium hydroxide. Calcium carbonate reacts with sulfur dioxide to form calcium sulfite (calcium sulfate(IV)):

$$CaCO_3(s) + SO_2(g) \rightarrow CaSO_3(s) + CO_2(g)$$
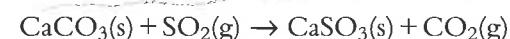
Nature of science

Acid rain is a problem that has been created by industrialisation. The work of chemists is vital in reducing the impact of acid rain by developing processes to limit the amounts of acidic gases released into the atmosphere. The problem of acid rain cannot however just be solved by scientists and it requires cooperation between scientists and politicians at a national and international level.

? Test yourself

21 Explain why rain is naturally acidic.
22 Give the formulas of two acids that arise from human activities and that are present in acid rain.

As with other equilibrium constants, the value of K_a depends on the temperature.

In general, for the dissociation of acid, HA:

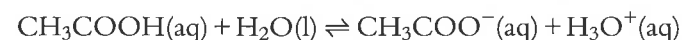$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

The expression for the acid dissociation constant is:

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

$K_a = 10^{-pK_a}$

8.7 Calculations involving acids and bases (HL)

The acid dissociation constant – K_a

Consider the dissociation of ethanoic acid:

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

We can write an equilibrium expression for the dissociation of an acid:

$$K_c = \frac{[CH_3COO^-(aq)][H_3O^+(aq)]}{[CH_3COOH(aq)][H_2O(l)]}$$

However, the reaction occurs in aqueous solution, and so the concentration of water is very much higher than the other concentrations and is essentially constant ($55.5 \, mol \, dm^{-3}$). This can be incorporated in the equilibrium expression:

$$K_c \times [H_2O(l)] = \frac{[CH_3COO^-(aq)][H_3O^+(aq)]}{[CH_3COOH(aq)]}$$

$K_c \times [H_2O(l)]$ is a new constant called the **acid dissociation constant** (or acid ionisation constant) and is given the symbol K_a. So we can write:

$$K_a = \frac{[CH_3COO^-(aq)][H_3O^+(aq)]}{[CH_3COOH(aq)]}$$

The value of K_a for ethanoic acid at 25 °C is 1.74×10^{-5}.

If we write the dissociation of ethanoic acid as:

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

we can write an equilibrium expression for the dissociation of the acid as:

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

This is entirely equivalent to the expression above.

Weak acids dissociate partially, and different weak acids dissociate to different extents. The acid dissociation constant is a measure of the extent to which an acid dissociates. The stronger the acid, the more it dissociates and the higher the value of K_a (the concentrations on the top of the expression are larger and that on the bottom is smaller).

pK_a

Acid dissociation constants can be expressed in a more convenient form by taking the negative logarithm to base 10 of K_a:

$$pK_a = -\log_{10} K_a$$

A low value of K_a corresponds to a high value of pK_a and vice versa, so that the lower a pK_a value is the stronger the acid (Table **8.4**).

You can think about this in the same way as for pH – the lower the pH value, the higher the $[H^+(aq)]$.

Acid	Formula	K_a	pK_a
hydrofluoric acid	HF	5.62×10^{-4}	3.25
benzoic acid	C_6H_5COOH	6.31×10^{-5}	4.20
propanoic acid	CH_3CH_2COOH	1.35×10^{-5}	4.87
chloric(I) acid	HOCl	3.72×10^{-8}	7.43
hydrocyanic acid	HCN	3.98×10^{-10}	9.40

Table 8.4 K_a and pK_a values of some acids – decreasing in strength downwards.

The acids in Table **8.4** are arranged in order of strength – HF is the strongest acid and dissociates to the greatest extent; HCN is the weakest acid and dissociates to the smallest extent in aqueous solution.

The higher the value of K_a, the stronger the acid. The lower the value of pK_a the stronger the acid.

K_a and pK_a are better measures of acid strength than pH because their values do not depend on the concentration of the acid – K_a and pK_a depend only on temperature.

Worked examples

8.3 Calculate the K_a value for methanoic acid at 25 °C if a $0.100 \, mol \, dm^{-3}$ solution dissociates to give a hydrogen ion concentration of $4.13 \times 10^{-3} \, mol \, dm^{-3}$.

Methanoic acid dissociates according to the equation: $HCOOH(aq) \rightleftharpoons HCOO^-(aq) + H^+(aq)$

If we consider the situation before dissociation occurs we have:

$$HCOOH(aq) \rightleftharpoons HCOO^-(aq) + H^+(aq)$$

initial concentration / $mol \, dm^{-3}$:   0.100   0   0
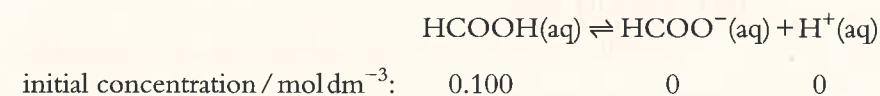
At equilibrium the concentration of H^+ ions is $4.13 \times 10^{-3} \, mol \, dm^{-3}$. To produce $4.13 \times 10^{-3} \, mol \, dm^{-3}$ H^+, $4.13 \times 10^{-3} \, mol \, dm^{-3}$ HCOOH must dissociate. The concentration of HCOOH at equilibrium is thus $0.100 - 4.13 \times 10^{-3}$, i.e. $9.59 \times 10^{-2} \, mol \, dm^{-3}$.

Because one molecule of HCOOH dissociates to produce one H^+ ion and one $HCOO^-$ ion, the concentration of $HCOO^-$ at equilibrium is the same as that of H^+.

we are assuming that we can ignore any contribution to $[H^+(aq)]$ from the dissociation of water.

So the equilibrium concentrations are:

$$HCOOH(aq) \rightleftharpoons HCOO^-(aq) + H^+(aq)$$

equilibrium concentration / $mol \, dm^{-3}$: 9.59×10^{-2} 4.13×10^{-3} 4.13×10^{-3}
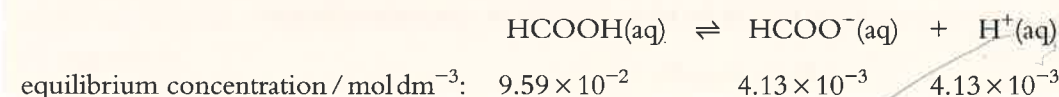
These values can be put into the expression for K_a:

$$K_a = \frac{[HCOO^-(aq)][H^+(aq)]}{[HCOOH(aq)]} = \frac{(4.13 \times 10^{-3}) \times (4.13 \times 10^{-3})}{(9.59 \times 10^{-2})} = 1.78 \times 10^{-4}$$

If the degree of dissociation is very small compared with the concentration of the acid, the above calculation may be simplified, as shown in the next example.

8.4 Calculate the K_a value for HCN(aq) at 25 °C if a 0.500 mol dm^{-3} solution dissociates to give a hydrogen ion concentration of 1.41×10^{-5} mol dm^{-3}.

The dissociation of HCN is represented by the equation: $HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$

The concentration of CN$^-$ at equilibrium will be the same as that of H$^+$. We will make the assumption that, because the dissociation of the acid is so small, the concentration of HCN at equilibrium is essentially the same as the initial concentration. We can now substitute these values into the expression for K_a:

$$K_a = \frac{[CN^-(aq)][H^+(aq)]}{[HCN(aq)]} = \frac{(1.41 \times 10^{-5}) \times (1.41 \times 10^{-5})}{(0.500)} = 3.98 \times 10^{-10}$$

This is the same as the literature value for K_a, and so it can be seen that the approximation works well when the degree of dissociation is so small. If we had made the same approximation in the calculation above on methanoic acid, the value obtained for K_a would have been 1.71×10^{-4}, which is reasonably close to the accepted value. This approximation will be discussed further below.

The base ionisation (dissociation) constant – K_b

Consider the ionisation of a weak base:

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

We can write an expression for the **base ionisation constant** (base dissociation constant), K_b:

$$K_b = \frac{[BH^+(aq)][OH^-(aq)]}{[B(aq)]}$$

As above, the reaction occurs in aqueous solution, so the concentration of water is very much higher than the other concentrations and is essentially constant. It is therefore omitted from the expression for K_b.

The value of K_b for ammonia is 1.78×10^{-5}. Similar to K_a for acids, K_b for bases provides a measure of the extent to which a base ionises, and hence the strength of the base.

pK_b

As for acids, the negative logarithm to base 10 of the base ionisation constant can be taken for a more convenient measure.

$$pK_b = -\log_{10} K_b$$

$K_b = 10^{-pK_b}$

> The higher the value of K_b, the more the base ionises and the stronger it is – the lower the value of pK_b, the stronger the base.

The K_b and pK_b values for some bases are shown in Table **8.5**. They are arranged in order of strength – dimethylamine is the strongest base and ionises to the greatest extent; phenylamine is the weakest base and ionises to the smallest extent in aqueous solution.

Base	Formula	K_b	pK_b
dimethylamine	$(CH_3)_2NH$	5.25×10^{-4}	3.28
methylamine	CH_3NH_2	4.37×10^{-4}	3.36
sodium carbonate	Na_2CO_3	2.09×10^{-4}	3.68
ammonia	NH_3	1.78×10^{-5}	4.75
phenylamine	$C_6H_5NH_2$	4.17×10^{-10}	9.38

Table 8.5 K_b and pK_b values for some bases – decreasing in strength downwards.
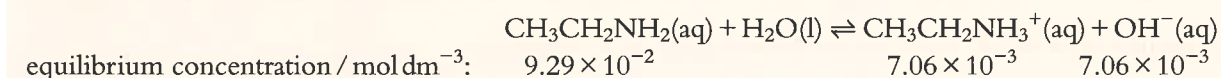
Worked example

8.5 Calculate the K_b value for ethylamine at 25 °C if a 0.100 mol dm^{-3} solution ionises to give a hydroxide ion concentration of 7.06×10^{-3} mol dm^{-3}.

The equation for the ionisation of ethylamine is:

$$CH_3CH_2NH_2(aq) + H_2O(l) \rightleftharpoons CH_3CH_2NH_3^+(aq) + OH^-(aq)$$
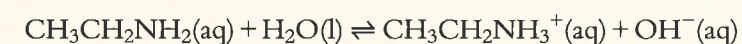
When one molecule of $CH_3CH_2NH_2$ reacts with water, it ionises to form one $CH_3CH_2NH_3^+$ ion and one OH$^-$ ion. This means that, if 7.06×10^{-3} mol dm^{-3} of OH$^-$ are present at equilibrium, they must have come from the ionisation of 7.06×10^{-3} mol dm^{-3} $CH_3CH_2NH_2$. The concentration of $CH_3CH_2NH_2$ at equilibrium is therefore $0.100 - 7.06 \times 10^{-3} = 9.29 \times 10^{-2}$ mol dm^{-3}. The concentration of OH$^-$ formed is the same as that of $CH_3CH_2NH_3^+$ (again, ignoring any contribution from the dissociation of water).

So at equilibrium, the concentrations are:

$$CH_3CH_2NH_2(aq) + H_2O(l) \rightleftharpoons CH_3CH_2NH_3^+(aq) + OH^-(aq)$$

equilibrium concentration / mol dm^{-3}: 9.29×10^{-2} 7.06×10^{-3} 7.06×10^{-3}

The expression for K_b is:

$$K_b = \frac{[CH_3CH_2NH_3^+(aq)][OH^-(aq)]}{[CH_3CH_2NH_2(aq)]}$$

The equilibrium concentrations can be substituted into this:

$$K_b = \frac{[7.06 \times 10^{-3}][7.06 \times 10^{-3}]}{[9.29 \times 10^{-2}]} = 5.37 \times 10^{-4}$$

As for the K_a calculation above, this can be simplified by making the approximation that the amount of ionisation of the base is small compared with its concentration, so the original concentration of the base could be used in the K_b expression.

Calculating the pH of a solution of a weak acid

A weak acid dissociates only partially, and therefore in order to calculate the pH we need to know how much the acid dissociates. This can be worked out using the K_a or pK_a value of the acid.

Worked example

8.6 Calculate the pH of a $0.100 \, \text{mol dm}^{-3}$ solution of ethanoic acid at $25\,^\circ\text{C}$.
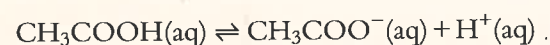The pK_a of ethanoic acid at $25\,^\circ\text{C}$ is 4.76.

$K_a = 10^{-pK_a}$ '2nd/SHIFT log' (-4.76) on the calculator

$\quad = 10^{-4.76}$

$\quad = 1.74 \times 10^{-5}$

The equation for the dissociation of ethanoic acid is:

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

and its equilibrium expression is:

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

Because one molecule of CH_3COOH dissociates to form one CH_3COO^- ion and one H^+ ion, the concentration of CH_3COO^- and H^+ ions in the solution will be equal:

$$[CH_3COO^-(aq)] = [H^+(aq)]$$

We will make the assumption that the dissociation of the acid is negligible compared with the concentration of the acid – so the concentration of the acid at equilibrium is the same as its initial concentration, $0.100 \, \text{mol dm}^{-3}$ in this case.

These terms, together with the K_a value, are substituted into the K_a expression:

$$1.74 \times 10^{-5} = \frac{[H^+(aq)]^2}{0.100}$$

$[H^+(aq)]^2 = 1.74 \times 10^{-5} \times 0.100 = 1.74 \times 10^{-6}$

$[H^+(aq)] = \sqrt{(1.74 \times 10^{-6})} = 1.32 \times 10^{-3} \, \text{mol dm}^{-3}$

Now, $pH = -\log_{10}[H^+(aq)]$

So $pH = -\log_{10}(1.32 \times 10^{-3})$

$\quad\quad = 2.88$

If c is the concentration of the acid, the hydrogen ion concentration can also be worked out using:

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

or the pH could be worked out using:

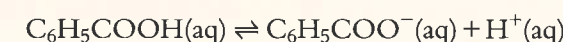$$pH = \tfrac{1}{2}(pK_a - \log_{10} c) \text{ or } pH = -\tfrac{1}{2}\log_{10}(c \times K_a)$$

Calculating K_a for a weak acid from its pH

Worked example

8.7 Calculate the value of the acid dissociation constant for benzoic acid if a $0.250 \, \text{mol dm}^{-3}$ solution has a pH of 2.40.

The equation for the dissociation of benzoic acid is:

$$C_6H_5COOH(aq) \rightleftharpoons C_6H_5COO^-(aq) + H^+(aq)$$

$$K_a = \frac{[C_6H_5COO^-(aq)][H^+(aq)]}{[C_6H_5COOH(aq)]}$$

$[H^+(aq)]$ can be worked out from the pH:

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

$[H^+(aq)] = 10^{-2.40} = 3.98 \times 10^{-3} \, \text{mol dm}^{-3}$

To produce $3.98 \times 10^{-3} \, \text{mol dm}^{-3} \, H^+$, $3.98 \times 10^{-3} \, \text{mol dm}^{-3} \, C_6H_5COOH$ must dissociate. The concentration of C_6H_5COOH at equilibrium is thus $0.250 - 3.98 \times 10^{-3} \, \text{mol dm}^{-3}$, i.e. $0.246 \, \text{mol dm}^{-3}$.

Because one molecule of C_6H_5COOH dissociates to produce one H^+ ion and one $C_6H_5COO^-$ ion, the concentration of $C_6H_5COO^-$ at equilibrium is the same as that of H^+.

The equilibrium concentrations are thus:

$$C_6H_5COOH(aq) \rightleftharpoons C_6H_5COO^-(aq) + H^+(aq)$$
equilibrium concentration / mol dm^{-3}: $\quad$ 0.246 $\quad\quad$ 3.98×10^{-3} $\quad$ 3.98×10^{-3}
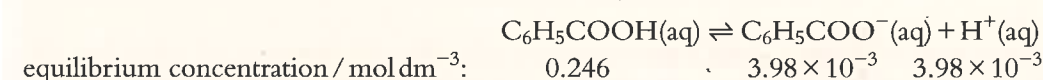
These values can be put into the expression for K_a:

$$K_a = \frac{[C_6H_5COO^-(aq)][H^+(aq)]}{[C_6H_5COOH(aq)]}$$

$$K_a = \frac{(3.98 \times 10^{-3}) \times (3.98 \times 10^{-3})}{0.246}$$

$$K_a = 6.44 \times 10^{-5}$$

If the approximation had been made that the effect of the dissociation of the acid on the concentration of the acid at equilibrium can be ignored, the answer 6.34×10^{-5} would have been obtained.

The answer 6.34×10^{-5} could also have been obtained using the equation:

$$K_a = \frac{10^{-2pH}}{c}$$

where c is the concentration of the acid.

Calculating the pOH or pH of a solution of a base

pOH

Calculating the pH of a solution of a base can be simplified using the idea of pOH.

$$pOH = -\log_{10}[OH^-(aq)]$$

Consider the expression for the ionic product constant for water:

$$K_w = [H^+(aq)][OH^-(aq)]$$

Working out $-\log_{10}$ for both sides gives:

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

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

We can rewrite this:

$$pK_w = pH + pOH$$

$pK_w = -\log_{10}K_w$
'p' stands for '$-\log_{10}$'

Now, the value of pK_w at 25 °C is $-\log_{10}1.0\times10^{-14}$, which is 14; so we can rewrite the equation above:

$$pH + pOH = 14$$

Worked example

8.8 Calculate the pH of $0.0500\,\text{mol}\,\text{dm}^{-3}$ sodium hydroxide solution at 25 °C.

NaOH is a strong base and ionises completely to form $0.0500\,\text{mol}\,\text{dm}^{-3}$ $OH^-(aq)$.

$$pOH = -\log_{10}(0.0500) = 1.30$$

At 25 °C, $pH + pOH = 14$

$$pH + 1.30 = 14$$

$$pH = 12.7$$

pH, pOH and neutrality

At 25 °C, neutral pH is 7. At that temperature, solutions that have a pH lower than 7 are acidic, and those that have a pH higher than 7 are alkaline.

Using pOH the situation is reversed – solutions with a pOH lower than 7 are alkaline, and those with a pOH higher than 7 are acidic.

Now $pH + pOH = pK_w$ so if $pH < pOH$ a solution is acidic, and if $pOH < pH$ the solution is alkaline.

In pure water (or a neutral solution), $pH = pOH$.

Calculating pH or pOH for a weak base

Because a weak base ionises only partially in aqueous solution, we must use K_b or pK_b to work out the concentration of OH^- ions present in a solution.
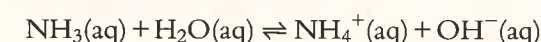
Worked example

8.9 Calculate pH and pOH of a $0.120\,\text{mol}\,\text{dm}^{-3}$ solution of ammonia, given that its pK_b is 4.75 at 25 °C.

$$K_b = 10^{-pK_b}$$

$$K_b = 10^{-4.75} = 1.78\times10^{-5}$$

The ionisation of ammonia involves:

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

$$K_b = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]}$$

One NH_3 molecule ionises to produce one NH_4^+ ion and one OH^- ion. This means that the concentration of NH_4^+ is equal to the concentration of OH^- and we can write:

$$K_b = \frac{[OH^-(aq)]^2}{[NH_3(aq)]}$$

We will make the approximation that the concentration of NH_3 at equilibrium is equal to the initial concentration – i.e. that the extent of ionisation of the base is negligible compared with its concentration. Therefore we take $[NH_3(aq)]$ as $0.120\,\text{mol}\,\text{dm}^{-3}$. Substituting this value and the value for K_b into the expression for K_b:

$$1.78\times10^{-5} = \frac{[OH^-(aq)]^2}{0.120}$$

$$[OH^-(aq)]^2 = 1.78\times10^{-5}\times0.120$$

$$= 2.14\times10^{-6}$$

Therefore, $[OH^-(aq)] = 1.46\times10^{-3}\,\text{mol}\,\text{dm}^{-3}$

and $pOH = -\log_{10}[OH^-(aq)]$

$$= -\log_{10}(1.46\times10^{-3})$$

$$= 2.84$$

But $pOH + pH = pK_w$

At 25 °C, $pOH + pH = 14$.

Therefore, $pH = 14 - 2.84$

$$= 11.16.$$

If c is the concentration of the base, the hydroxide ion concentration can also be worked out using:

$$[OH^-(aq)] = \sqrt{(c\times K_b)}$$

pOH can be worked out using:

$$pOH = -\tfrac{1}{2}\log_{10}(c\times K_b) \text{ or } pOH = \tfrac{1}{2}(pK_b - \log_{10}c)$$

The pH could be worked out using:

$$pH = 14 + \tfrac{1}{2}\log_{10}(c\times K_b) \text{ or } pH = 14 - \tfrac{1}{2}(pK_b - \log_{10}c)$$

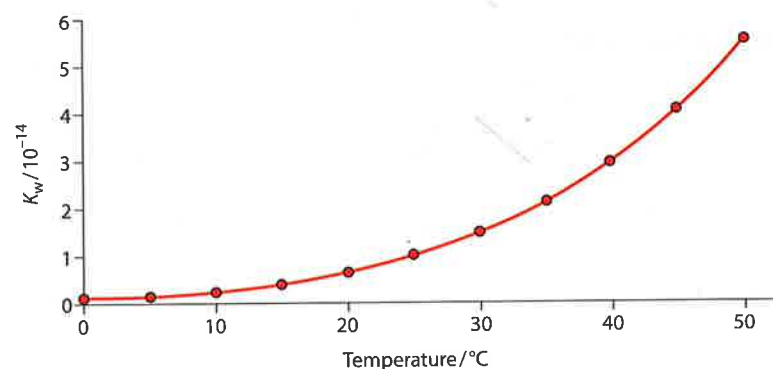## The variation of K_w with temperature

Like all other equilibrium constants, the value of K_w varies with temperature (Table **8.6** and Figure **8.14**). We can use the data in Table **8.6** to work out the pH of water at any temperature.

Temperature/°C	K_w
0	1.14×10^{-15}
5	1.86×10^{-15}
10	2.93×10^{-15}
15	4.52×10^{-15}
20	6.81×10^{-15}
25	1.01×10^{-14}
30	1.47×10^{-14}
35	2.09×10^{-14}
40	2.92×10^{-14}
45	4.02×10^{-14}
50	5.48×10^{-14}

Table 8.6 The variation of K_w with temperature.

Figure 8.14 The variation of K_w with temperature.

Worked example

8.10 Using the values in Table **8.6**, calculate the pH of water at 40 °C.

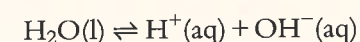From the table, the value of K_w at this temperature is 2.92×10^{-14}.

$$pK_w = -\log_{10}(2.92\times10^{-14}) = 13.53$$

$$pH + pOH = pK_w$$

$$pH + pOH = 13.53$$

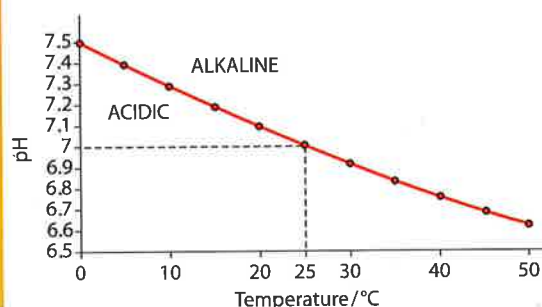Water dissociates according to the equation:

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

Because one H_2O molecule dissociates to form one H^+ ion and one OH^- ion in pure water, the concentration of H^+ ions is equal to the concentration of OH^- ions, and therefore $pH = pOH$.

So $2\times pH = 13.53$ and $pH = 6.77$

Therefore the pH of pure water at 40 °C is 6.77.

Figure 8.15 The variation of neutral pH with temperature.

This does not, however, mean that the water is acidic at 40 °C, and we must now modify our definition of 'neutral'. Pure water is neutral because $[H^+(aq)] = [OH^-(aq)]$. Because K_w equals 1.0×10^{-14} only at 25 °C, we can also see that pH 7 is neutral only at 25 °C!

The graph in Figure **8.15** shows the variation of neutral pH with temperature. Any pH value above the red line indicates an alkaline pH at that temperature; any pH below the line indicates an acidic pH at that temperature. So at 10 °C a pH of 7.1 is in the acidic region, below the line, and represents an acidic pH at this temperature!

A solution is neutral if $[H^+(aq)] = [OH^-(aq)]$; a solution is acidic if $[H^+(aq)] > [OH^-(aq)]$, and a solution is alkaline if $[OH^-(aq)] > [H^+(aq)]$.

When students first come across the idea of water having a pH lower than 7 at 40 °C and they are asked about it, the deductive reasoning that usually goes on is:

- all liquids with a pH lower than 7 are acidic
- at 40 °C water is a liquid with a pH lower than 7
- therefore water is acidic at 40 °C.

The conclusion of this reasoning is incorrect, but the argument is valid. The problem is, of course, with the first premise which, we have just learnt, is incorrect. Can you reword the first premise to make it true and construct a valid argument?

There is also another problem here – when I first thought about demonstrating this argument, I wanted to write the first premise as 'all solutions with pH less than 7 are acidic'. Why did I choose the word 'liquid' instead and does this introduce any extra difficulties in trying to come up with a completely true version of the first premise?

Another problem we encounter the first time we come across the idea of water having a pH other than 7 is, of course, that we 'know' that the neutral pH is 7 because we have been told it from an early age – it is even stated earlier in this chapter! The idea of water having a pH of anything other than 7 goes against everything we have learnt. If you obtained this result experimentally using a pH meter before you learnt about the theory of pH, would you dismiss the result as wrong (the pH meter had been poorly calibrated!) and ignore it?

The pH of strong acids/bases at different temperatures

It can be seen from the above discussion that pH varies with temperature and therefore we can work out the pH of any solution given the value of K_w or pK_w at that temperature.

Worked example

8.11 Calculate the pH of $0.0500\,mol\,dm^{-3}$ sodium hydroxide solution at 50 °C given that $pK_w = 13.3$ at this temperature.

$$pOH = -\log_{10}(0.0500) = 1.30$$

$$pH + pOH = pK_w$$

$$pH + pOH = 13.3$$

$$pH + 1.30 = 13.3$$

$$pH = 12.0 \text{ (it is 12.7 at 25 °C)}$$

23 HA to HF are all weak acids.

   a Copy and complete the following table:

Acid	Concentration / mol dm^{-3}	[H$^+$]/ mol dm^{-3}	pH	K_a	pK_a
HA	0.0100	2.00×10^{-6}			
HB	0.200		4.70		
HC	0.500	2.50×10^{-4}			
HD	2.20×10^{-2}		5.20		
HE	0.250			3.72×10^{-8}	
HF	0.0300			4.96×10^{-6}	

   b Use the values in part **a** to arrange the acids in order of acid strength (strongest first).

24 B$_1$, B$_2$ and B$_3$ are weak bases.

   a Copy and complete the table:

Base	Concentration of base / mol dm^{-3}	[OH$^-$] / mol dm^{-3}	K_b	pK_b
B$_1$	0.100	1.33×10^{-3}		
B$_2$	0.250		5.75×10^{-5}	
B$_3$	0.0200	4.70×10^{-4}		

   b Arrange the bases in order of increasing strength (weakest first).

25 Arrange the following acids in order of increasing strength (weakest first):

Acid	pK_a
HOCl	7.4
HClO$_2$	2.0

Acid	K_a
HOI	3.0×10^{-11}
HNO$_2$	4.6×10^{-4}

26 Calculate pH values for the following solutions:

   a a 0.0200 mol dm^{-3} solution of propanoic acid, given that the pK_a value at 25 °C is 4.87.

   b a 0.500 mol dm^{-3} solution of HCN, given that the pK_a value at 25 °C is 9.40.

   c a 0.002 50 mol dm^{-3} solution of phenol (C$_6$H$_5$OH), given that the pK_a value at 25 °C is 10.00.

27 Calculate the pH of pure water at each of the following temperatures

   a at 5 °C, K_w is 1.86×10^{-15}

   b at 35 °C, K_w is 2.09×10^{-14}

   c at 100 °C, K_w is 5.13×10^{-13}

28 Calculate the pOH of the following solutions at 25 °C:

   a 0.0300 mol dm^{-3} KOH

   b 0.500 mol dm^{-3} NaOH

   c 0.0200 mol dm^{-3} HCl

29 Calculate the pH values for the following solutions:

   a a 0.0500 mol dm^{-3} solution of ethylamine (CH$_3$CH$_2$NH$_2$) at 25 °C, given that the K_b value is 5.37×10^{-4} at that temperature.

   b a 0.0100 mol dm^{-3} solution of phenylamine (C$_6$H$_5$NH$_2$) at 25 °C, given that the K_b value is 4.17×10^{-10} at that temperature.

30 Calculate the pH of each of the following solutions at the given temperature:

   a 0.1000 mol dm^{-3} NaOH at 40 °C (pK_w = 13.53)

   b 0.1000 mol dm^{-3} HCl at 30 °C (pK_w = 13.83)

   c 0.02000 mol dm^{-3} KOH at 30 °C (pK_w = 13.83)

Strong acids so [yes dissocide completely]

The relationship between K_a and K_b

Consider the equilibria for an acid HA and its conjugate base A$^-$:

$$HA(aq) \rightleftharpoons A^-(aq) + H^+(aq) \qquad \text{equation 1}$$

$$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq) \qquad \text{equation 2}$$
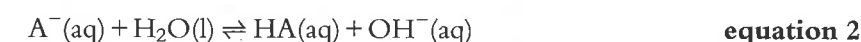
We can write the K_a expression for equation 1:

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

and the K_b expression for equation 2:

$$K_b = \frac{[HA(aq)][OH^-(aq)]}{[A^-(aq)]}$$

If we multiply K_a by K_b, we get:

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

$$K_a \times K_b = [H^+(aq)] \times [OH^-(aq)]$$

But $[H^+(aq)] \times [OH^-(aq)] = K_w$, so we can write:

$$K_a \times K_b = K_w$$

This relationship works only for a conjugate acid–base pair, e.g. for NH$_4^+$ ($K_a = 5.62 \times 10^{-10}$) and for NH$_3$ ($K_b = 1.78 \times 10^{-5}$):

$$K_a \times K_b = 5.62 \times 10^{-10} \times 1.78 \times 10^{-5} = 1.00 \times 10^{-14}$$

which is the value for K_w at 25 °C.

If we take negative logarithms to base 10 of each side in the expression $K_a \times K_b = K_w$, we get the relationship:

$$pK_a + pK_b = pK_w$$

At 25 °C the value of pK_w is 14, so, at 25 °C, pK_a + pK_b = 14.

The pK_a for ethanoic acid (CH$_3$COOH) is 4.76 and the pK_b for its conjugate base, the ethanoate ion (CH$_3$COO$^-$), is 9.24 at 25 °C.

Certain terms cancel.

$4.76 + 9.24 = 14$

The relationship between the strength of an acid and the strength of its conjugate base

For a conjugate acid–base pair, pK_a + pK_b = pK_w (or $K_a \times K_b = K_w$). This means that the lower the value of pK_a for an acid, the higher the value of pK_b for its conjugate base. A lower value of pK_a indicates a stronger acid and a higher value of pK_b indicates a weaker base. This leads to the conclusion that was discussed earlier:

The stronger the acid, the weaker its conjugate base.

The lower the value of pK_a, the stronger the acid.

The lower the value of pK_b, the stronger the base.

Acid	pK_a		Conjugate base	pK_b	
HF	3.25		F^-	10.75	
C_6H_5COOH	4.20		$C_6H_5COO^-$	9.80	
CH_3CH_2COOH	4.87	increasing strength	$CH_3CH_2COO^-$	9.13	increasing strength
HOCl	7.43		OCl^-	6.57	
HCN	9.40		CN^-	4.60	

Table 8.7 The relationship between the strength of an acid and its conjugate base.

HCN is the weakest acid in Table **8.7** and has the strongest conjugate base. HCN has very little tendency to dissociate, according to the equation:

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$$
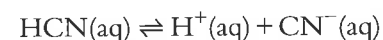
and CN^- has a strong tendency to react with water to re-form the parent acid:

$$CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$$
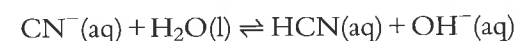
Nature of science

We started the chapter with a qualitative discussion of acids and bases and have now considered a mathematical description of acidity. It is the goal of many areas of science to describe natural phenomena mathematically. Depending on the sophistication of the model, more or fewer assumptions/approximations are used. The development of more sophisticated equipment, such as the pH meter, can allow testing and refinement of the models.

? Test yourself

31 Copy and complete the following table, which contains values measured at 25 °C. The first row has been done for you.

Acid	K_a	pK_a	Conjugate base	K_b	pK_b
HCN	3.98×10^{-10}	9.40	CN^-	2.51×10^{-5}	4.60
HF	5.62×10^{-4}				
HIO_3		0.8			
NH_4^+					4.75
			CH_3COO^-	5.75×10^{-10}	
		10.64	CH_3NH_2		

## 8.8 pH curves (HL)

8.8.1 Acid–base titrations

We met the use of acid–base titrations in Topic **1** for determining the concentration of one solution by reacting it with another that we know the concentration of (a standard solution). The pH of the mixture does not vary linearly during titration and just how it changes during the process depends on whether the reactants are strong or weak acids/bases and what their concentrations are. Even when equivalent numbers of moles of acid and alkali have been added the pH is not necessarily 7. This is why different indicators, which change colour at different pH values, are required for different titrations – for instance, phenolphthalein changes colour around pH 9 and is usually used for weak acid–strong base titrations. This is explained in more detail on page **352**.

Here we will look at **titration curves**, which show how pH varies during titrations involving different combinations of strong and weak acids and bases. The pH can be monitored during a titration by using a pH meter or a pH probe attached to a data logger (Figure **8.16**).

Strong acid–strong base

The titration curve (pH curve) for adding $0.100 \, mol \, dm^{-3}$ sodium hydroxide solution to $25.0 \, cm^3$ of $0.100 \, mol \, dm^{-3}$ hydrochloric acid is shown in Figure **8.17**.
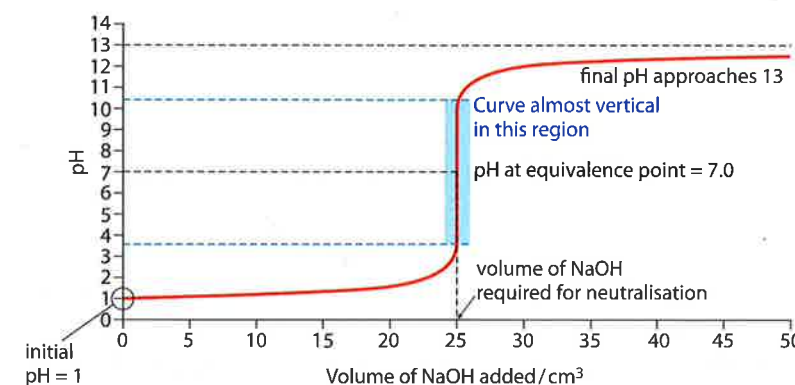
The reaction that occurs is:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$
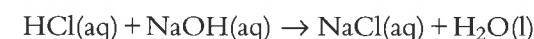
The initial pH is 1.0 because the initial solution is $0.100 \, mol \, dm^{-3}$ hydrochloric acid. Hydrochloric acid is a strong acid and dissociates completely:

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

The concentration of H^+ ions is $0.100 \, mol \, dm^{-3}$ and the $pH = -\log_{10} 0.10$, i.e. 1.00.

Figure 8.17 A strong acid–strong base titration curve.

Learning objectives

- Sketch titration curves (pH curves) for titrations involving any combination of strong and weak acids and bases
- Explain the important features of titration curves
- Understand how to work out pK_a or pK_b values from a titration curve
- Explain how an acid–base indicator works
- Understand what is meant by the pH range of an indicator
- Select a suitable indicator for a titration
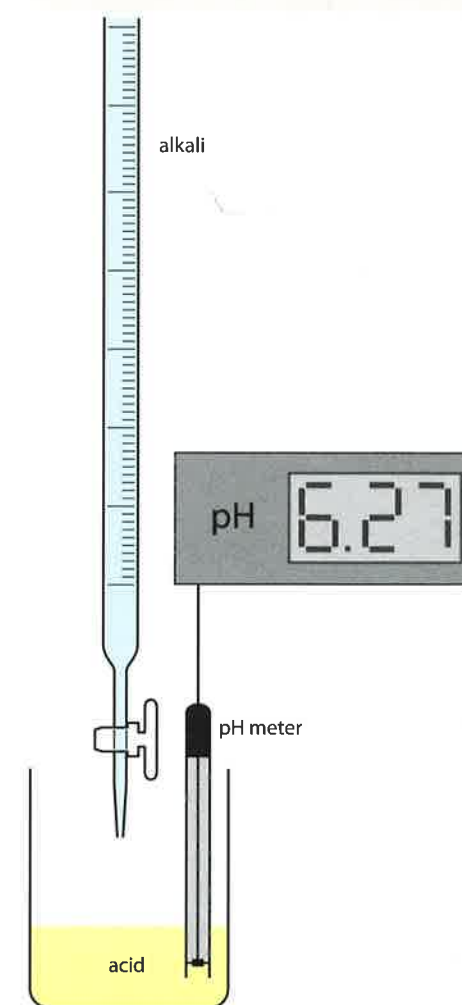
Figure 8.16 This experimental set-up could be used to track the pH of a solution in a titration.

From Figure **8.17** it can be seen that as NaOH is added, the pH initially changes very little. The pH after $20.0\,cm^3$ of NaOH has been added is 1.95, so adding $20.0\,cm^3$ of the sodium hydroxide has changed the pH of the solution by less than 1 unit. This is partly a consequence of the fact that the $H^+(aq)$ ion concentration is reasonably high in this region and therefore adding NaOH does not affect the overall pH very much. However, it also arises from the nature of the log scale – the $[H^+(aq)]$ in this region decreases by about $0.09\,mol\,dm^{-3}$ from $0.100\,mol\,dm^{-3}$ to $0.010\,mol\,dm^{-3}$, but a ten fold change in the $[H^+(aq)]$ corresponds to a change in pH of only one unit.

The pH then increases much more rapidly, and between a pH of about 3.5 and 10.5 the curve is virtually vertical. In this region (shaded on the graph), the addition of about $0.3\,cm^3$ of NaOH causes the pH to change by 7 units. In this region $[H^+(aq)]$ is low and adding NaOH has a larger effect on the pH. The fact that this is a log scale, however, magnifies the effect – in this region the $[H^+(aq)]$ actually decreases by only about $0.000\,31\,mol\,dm^{-3}$, but because it decreases from $3.15 \times 10^{-4}\,mol\,dm^{-3}$ to $3.15 \times 10^{-11}\,mol\,dm^{-3}$, the pH changes by 7 units.

The **equivalence point** is the point at which equivalent numbers of moles of acid and base have been added. The pH at the equivalence point for a strong acid–strong base titration is 7.0.

In this case, because the concentrations of the acid and base are equal, the equivalence point occurs when equal volumes of the acid and base have been added.

After this region, the pH changes only gradually again, and as more and more NaOH is added the pH gets closer to 13, which is the pH of $0.100\,mol\,dm^{-3}$ NaOH(aq). All the acid has been neutralised and the OH^- ions are in excess in this region. As more and more NaOH is added, the solution resembles more and more closely the original NaOH solution (when $200\,cm^3$ have been added the pH is 12.89).

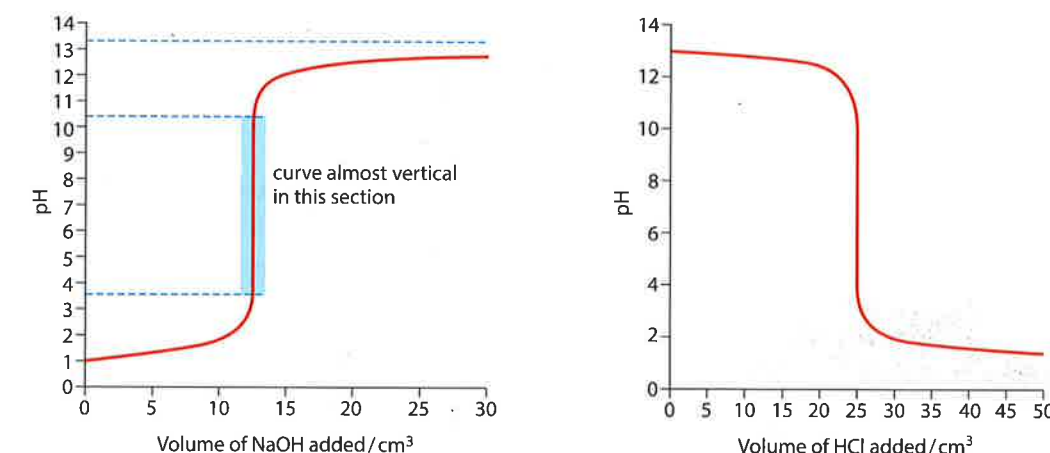### Variations on strong acid–strong base titrations

If, instead of adding $0.100\,mol\,dm^{-3}$ NaOH to $25\,cm^3$ of $0.100\,mol\,dm^{-3}$ HCl, we add $0.200\,mol\,dm^{-3}$ NaOH then we would get the titration curve shown in Figure **8.18a**. The equivalence point would now occur when $12.5\,cm^3$ of the alkali has been added. The initial pH would be the same and the pH at the equivalence point still 7.0, but the final pH will tend towards 13.3, the pH of $0.200\,mol\ dm^{-3}$ NaOH(aq).

If we used $1.00\,mol\,dm^{-3}$ HCl and $1.00\,mol\,dm^{-3}$ NaOH for the titration:
- the initial pH would be lower (0.0)
- the steep part would be longer
- the final pH would tend towards 14.0 – the pH of $1.00\,mol\,dm^{-3}$ NaOH(aq)
- the pH at the equivalence point would still be 7.0.

If we had performed the original titration the other way round, adding the acid to the alkali, the curve would have been reversed, as shown in Figure **8.18b**. The initial pH would have been 13.0 – the pH of $0.100\,mol\,dm^{-3}$ NaOH(aq) – and the curve would tend towards 1.0, the pH of $0.100\,mol\,dm^{-3}$ HCl(aq).

Note: the equivalence point is **not** the same as the end point – the end point will be discussed in the section on indicators (page **349**).

Figure 8.18 Titration curves: **a** adding $0.200\,mol\,dm^{-3}$ NaOH to $25\,cm^3$ of $0.100\,mol\,dm^{-3}$ HCl; **b** adding $0.100\,mol\,dm^{-3}$ HCl to $25\,cm^3$ of $0.100\,mol\,dm^{-3}$ NaOH.

Calculating the points on a strong acid–strong base titration curve

Consider again the original titration, i.e. the addition of $0.100\,mol\,dm^{-3}$ sodium hydroxide solution to $25.0\,cm^3$ of $0.100\,mol\,dm^{-3}$ hydrochloric acid (Figure **8.17**). We will look at how each point on the titration curve can be calculated.

Initial pH (no base added)
The initial pH is 1.00, because the initial solution is $0.100\,mol\,dm^{-3}$ hydrochloric acid. Hydrochloric acid is a strong acid and dissociates completely:

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

The concentration of H^+ ions is $0.100\,mol\,dm^{-3}$ and the $pH = -\log_{10} 0.100$, i.e. 1.00.

In $25.0\,cm^3$ of $0.100\,mol\,dm^{-3}$ HCl, the number of moles of H^+ ions is given by:

$$\text{no. moles} = \text{concentration} \times \text{volume in dm}^3$$

$$\text{no. moles of } H^+ = 0.100 \times \frac{25.0}{1000} = 2.50 \times 10^{-3}\,mol$$

Addition of $5.0\,cm^3$ of the base
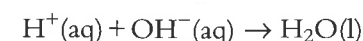The total volume of the solution is now:

$$25.0 + 5.0 = 30.0\,cm^3 \text{ or } 0.0300\,dm^3$$

The number of moles of OH^- ions in $5.0\,cm^3$ of solution is given by:

$$\text{no. moles of } OH^- = 0.100 \times \frac{5.0}{1000} = 5.0 \times 10^{-4}\,mol$$

These OH^- ions react with the H^+ ions in the acid solution according to the equation:

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

H^+ ions are in excess and 5.0×10^{-4} mol OH^- react with 5.0×10^{-4} mol H^+. The original number of moles of H^+ ions was 2.50×10^{-3}; therefore, if 5.0×10^{-4} mol react, the number of moles of H^+ ions left over in the solution is $2.50 \times 10^{-3} - 5.0 \times 10^{-4}$ or 2.00×10^{-3} mol.

This number of moles of H^+ is in $30.0\,cm^3$ of solution; therefore the concentration of H^+ ions in the solution is given by:

$$concentration = \frac{no.\ moles}{volume\ in\ dm^3}$$

$$[H^+(aq)] = \frac{2.00 \times 10^{-3}}{0.0300} = 6.67 \times 10^{-2}\,mol\,dm^{-3}$$

$$pH = -\log_{10}[H^+(aq)] = -\log_{10} 6.67 \times 10^{-2} = 1.18$$

This technique can be used to work out the pH of all the solutions up to the addition of just less than $25.0\,cm^3$ NaOH.

If the calculation is attempted for $25.0\,cm^3$ of NaOH added there is a problem because the number of moles of H^+ ions in the original solution was $2.50 \times 10^{-3}\,mol\,dm^{-3}$ and the number of moles of OH^- that is added is $2.50 \times 10^{-3}\,mol\,dm^{-3}$. These will react together completely so that the number of moles of H^+ left will be zero, but $-\log_{10}0$ does not exist! The problem has arisen because, in all of the above calculations, we have ignored any H^+ in the solution from the dissociation of water. In most cases we are totally justified in ignoring this. For instance, at $20.0\,cm^3$ of NaOH added, the concentration of H^+ ions in the solution from the hydrochloric acid is $0.0111\,mol\,dm^{-3}$, whereas that from the dissociation of water is $9.00 \times 10^{-13}\,mol\,dm^{-3}$ – the dissociation of water accounts for $8.1 \times 10^{-9}\%$ of the H^+ ion concentration of the solution. Even at $24.999\,cm^3$ of NaOH added, this percentage has only risen to about 0.25%.

However, at $25.0\,cm^3$ of NaOH added, the H^+ ion concentration of the solution is entirely due to the dissociation of water and the H^+ ion concentration is $1.00 \times 10^{-7}\,mol\,dm^{-3}$. So the pH of the solution is 7.0.

Beyond adding $25.0\,cm^3$ of NaOH, the calculation changes slightly because the NaOH is in excess. Let us consider the situation when $30.0\,cm^3$ of NaOH has been added. The total volume of the solution is:

$$25.0 + 30.0 = 55.0\,cm^3\ or\ 0.0550\,dm^3$$

The number of moles of OH^- ions in $30.0\,cm^3$ of solution is given by:

$$no.\ moles\ of\ OH^- = 0.100 \times \frac{30.0}{1000} = 3.00 \times 10^{-3}\,mol$$

These OH^- ions reacts with the H^+ ions in the solution according to the equation:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$
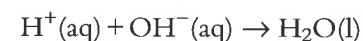
The original number of moles of H^+ ions was 2.50×10^{-3} mol.

The number of moles of OH^- in excess is:

$$3.00 \times 10^{-3} - 2.50 \times 10^{-3} = 5.0 \times 10^{-4}\,mol$$

$$concentration = \frac{no.\ moles}{volume\ in\ dm^3}$$

$$[OH^-(aq)] = \frac{5.0 \times 10^{-4}}{0.0550} = 9.09 \times 10^{-3}\,mol\,dm^{-3}$$

$$pOH = -\log_{10}[OH^-(aq)]$$

$$pOH = -\log_{10} 9.09 \times 10^{-3} = 2.04$$

At $25\,°C$, $pH + pOH = 14$. Therefore, $pH = 12.0$ (to three significant figures). Table **8.8** lists the pH values at different stages of the strong acid–strong base titration.

Weak acid–strong base

Let us consider adding $0.100\,mol\,dm^{-3}$ NaOH to $25\,cm^3$ of $0.100\,mol\,dm^{-3}$ CH_3COOH (ethanoic acid) ($K_a = 1.74 \times 10^{-5}$). The titration curve is shown in Figure **8.19**.
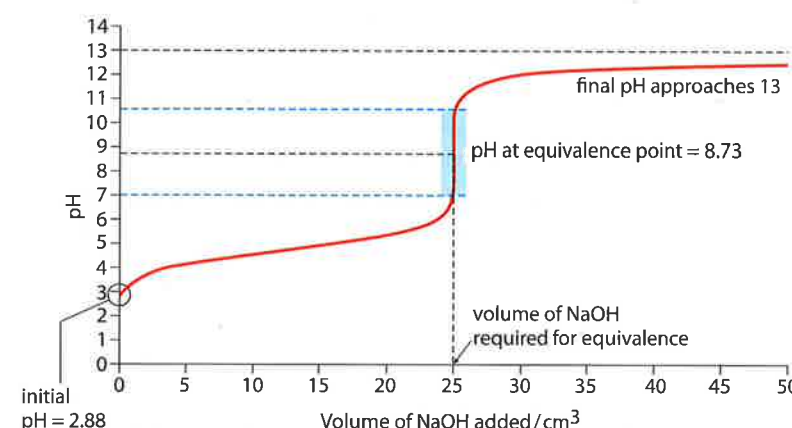

Figure 8.19 A titration curve for adding $0.100\,mol\,dm^{-3}$ NaOH to $25\,cm^3$ of $0.100\,mol\,dm^{-3}$ CH_3COOH.

The initial pH can be calculated using the K_a value for ethanoic acid and the method given on page **332**.

The equivalence point is reached when equal numbers of moles of acid and alkali have been added. As the concentrations of the acid and bases are the same, this occurs when the same volumes have been added (that is, when $25.0\,cm^3$ of sodium hydroxide has been added). The pH at the equivalence point is not 7, however – it is greater than 7.

The equation for the reaction is:

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$
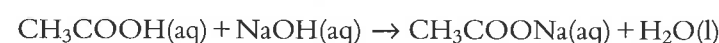
When equivalent amounts of ethanoic acid and sodium hydroxide have been added, a solution of sodium ethanoate ($CH_3COONa(aq)$) has been

pH values when 25.00 cm³ of 0.1000 mol dm⁻³ HCl is titrated with 0.1000 mol dm⁻³ NaOH	
Volume of NaOH added / cm³	pH
0.00	1.000
5.00	1.176
10.00	1.368
15.00	1.602
20.00	1.954
21.00	2.061
22.00	2.195
23.00	2.380
24.00	2.690
24.50	2.996
24.90	3.698
24.95	4.000
24.99	4.699
24.995	5.000
24.999	5.699
25.00	7.000
25.01	9.301
25.10	10.300
25.50	10.996
26.00	11.292
30.00	11.959
35.00	12.222
40.00	12.363
50.00	12.523
60.00	12.615
100.00	12.778
200.00	12.891

Table 8.8 Progressive addition of base and how the pH changes.

Remember – the weaker the acid, the stronger the conjugate base.

formed. The CH_3COO^- ion is the conjugate base of the weak acid CH_3COOH, and so, acting as a base, will react with some water molecules to accept a proton according to the equilibrium:

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$
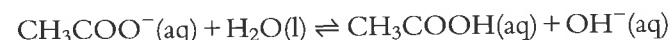
This reaction increases the concentration of OH^- ions in the solution and the pH at the equivalence point is therefore higher than 7.

The steep part of the curve, where it is virtually vertical, is more in the alkaline region than in the acidic region of the graph. As more and more NaOH is added, the pH approaches 13 – the pH of pure $0.100\,mol\,dm^{-3}$ NaOH.

In Figure 8.20, the weak acid–strong base titration curve is compared with a strong acid–strong base titration curve.
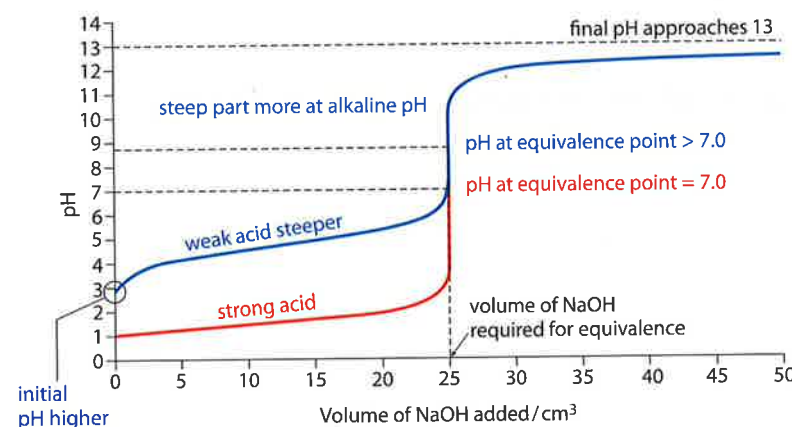

Figure 8.20 Comparison of a weak acid–strong base titration curve (blue) with a strong acid–strong base titration curve (red).

Note that the strength of the acid does not affect the volume of base required to reach the equivalence point for a titration. The volume of base required to reach the equivalence point depends only on the original volume of acid used, the concentration of the acid and the concentration of the base.

There are some important differences between strong acid–strong base titration curve and a weak acid–strong base titration curve. For a weak acid–strong base titration:

- The initial pH is higher. The weak acid is only partially dissociated.
- The initial part of the curve, up to a volume of about $24\,cm^3$ NaOH added, is steeper. Because the weak acid is only partially dissociated, the concentration of H^+ ions in the solution is lower, and adding a certain volume of NaOH has a greater relative effect on the pH than for a strong acid, in which the concentration of H^+ ions is higher.
- The steep part of the curve is more in the alkaline region.
- The pH at the equivalence point is higher than 7.

Determination of pK_a from a titration curve

The pK_a value for a weak acid can be determined experimentally by constructing a titration curve.

In the above example of the titration of $0.100\,mol\,dm^{-3}$ ethanoic acid with $0.100\,mol\,dm^{-3}$ NaOH, $25.0\,cm^3$ of NaOH is required to reach the equivalence point. Here we will consider the point in the titration when half this amount of NaOH has been added, i.e. $12.5\,cm^3$.

The equation for the reaction is:

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$
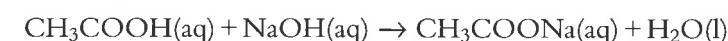
When $12.5\,cm^3$ of NaOH has been added, half of the CH_3COOH has been converted to CH_3COONa, and therefore the concentrations of CH_3COOH and CH_3COONa are equal. This can be seen if we work out the number of moles of each species:

$$\text{no. moles of } CH_3COOH \text{ originally in solution} = \frac{25.0}{1000} \times 0.1$$
$$= 2.50 \times 10^{-3}\,mol$$

$$\text{no. moles of NaOH added} = \frac{12.5}{1000} \times 0.1 = 1.25 \times 10^{-3}\,mol$$

$1.25 \times 10^{-3}\,mol$ NaOH will react with $1.25 \times 10^{-3}\,mol$ CH_3COOH to form $1.25 \times 10^{-3}\,mol$ CH_3COONa. There were originally $2.50 \times 10^{-3}\,mol$ CH_3COOH, and if $1.25 \times 10^{-3}\,mol$ reacted that leaves $1.25 \times 10^{-3}\,mol$ CH_3COOH in the reaction mixture – i.e. the same number of moles as CH_3COONa.

The expression for K_a is:

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

Because the concentration of CH_3COO^- is equal to the concentration of CH_3COOH, we can write:

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

and if we take $-\log_{10}$ of both sides, we get pK_a = pH. So at the half-equivalence point we can read the value of pK_a from the graph shown in Figure 8.21.

Strong acid–weak base titrations

Let us consider adding $0.100\,mol\,dm^{-3}$ $NH_3(aq)$ to $25\,cm^3$ $0.100\,mol\,dm^{-3}$ HCl(aq) (Figure 8.22). The pH at the equivalence point for a strong acid–weak base titration is at a pH lower than 7. At the equivalence point the NH_3 has reacted with HCl to form NH_4Cl:

$$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$$
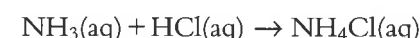
Exam tip
This seems to come up a lot in examinations!

Note: $[CH_3COONa(aq)]$ is equal to $[CH_3COO^-(aq)]$, as the ionic salt is fully dissociated in solution.
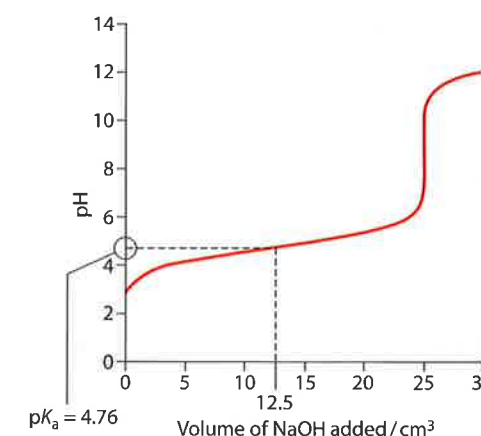

Figure 8.21 The pK_a value of the acid is equal to the pH at the half-equivalence point.
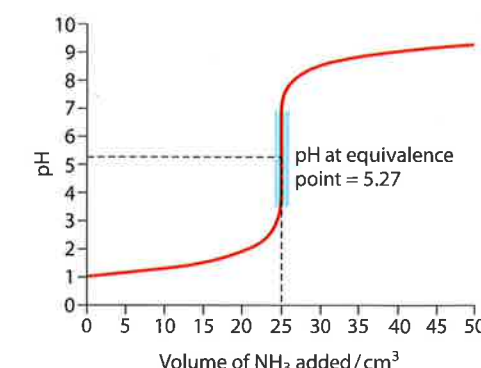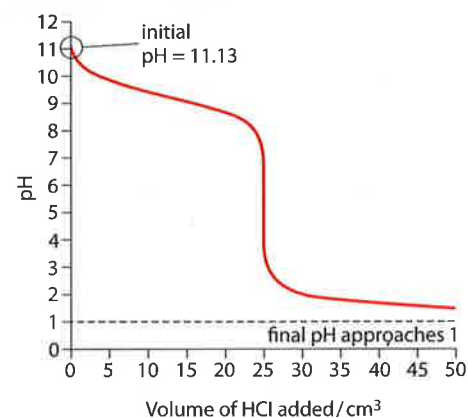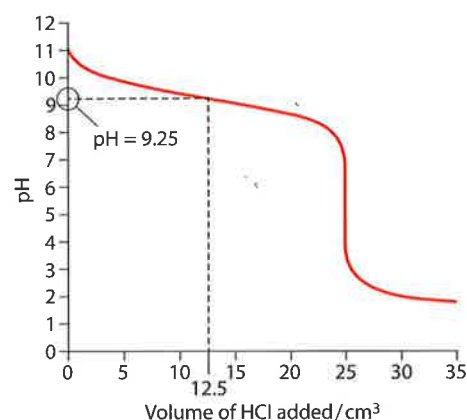

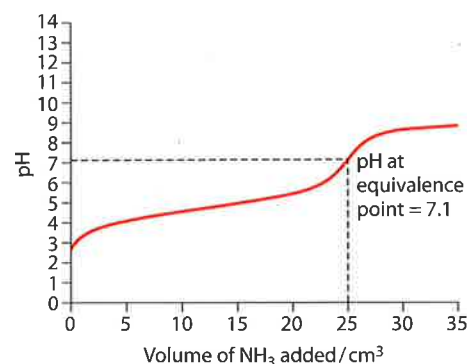**Figure 8.22** A strong acid–weak base titration curve.

Figure 8.23 Titration curve for adding a weak base to a strong acid.

> When a strong acid is added to a weak base, $pK_b = pOH$ at the half equivalence point.

Figure 8.24 pK_b can be obtained from a strong acid–weak base titration curve.

**Figure 8.25** A weak acid–weak base titration curve.

The ammonium ion is, however, the conjugate acid of a weak base and as such will dissociate to a certain extent in aqueous solution according to the equation:

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$$

So the concentration of H^+ ions in the solution is increased, and the pH is lower than 7.

The titration could also have been performed the other way around – that is, by adding hydrochloric acid to the ammonia solution. The titration curve obtained is shown in Figure **8.23**. The initial pH can be worked out using the K_b value of ammonia, as already described.

At the half–equivalence point of this titration, 12.5 cm³ of HCl has been added. The equilibrium that exists in this solution is:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
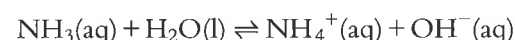
The expression for K_b is:

$$K_b = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]}$$

When 12.5 cm³ of HCl has been added, half of the NH_3 will have been converted into NH_4^+, and so the concentration of NH_3 will be equal to the concentration of NH_4^+.

$$K_b = \frac{[\cancel{NH_4^+(aq)}][OH^-(aq)]}{[\cancel{NH_3(aq)}]}$$

Therefore, at the half equivalence point: $K_b = [OH^-]$.

Taking $-\log_{10}$ of both side we get: $pK_b = pOH$.

At 25 °C, $pH + pOH = 14$, so, at the half equivalence point, $14 - pH = pK_b$. So we can thus work out the pK_b for ammonia from the graph in Figure **8.24**.

The pH at the half–equivalence point is 9.25, so the pK_b of ammonia is given by:

$$14 - 9.25 = pK_b$$

pK_b for ammonia is 4.75.

Weak acid–weak base

An example of titration of a weak acid and a weak base is the addition of 0.100 mol dm⁻³ NH_3(aq) to 25.0 cm³ of 0.100 mol dm⁻³ CH_3COOH (Figure **8.25**).

There is no very steep (almost vertical) part in this titration curve, and the change in pH throughout the titration is more gradual than in the other titrations we have considered.

The pH at the equivalence point may be lower than 7 or higher than 7, depending on the relative strength of the acid and the base. In this case, ethanoic acid ($K_a = 1.74 \times 10^{-5}$) is very similar in strength to ammonia

($K_b = 1.78 \times 10^{-5}$), and the pH at the equivalence point is very close to 7.0 (it is just slightly higher than 7.0 because the base is very slightly stronger than the acid). If we had used a different acid, such as methanoic acid ($K_a = 1.78 \times 10^{-4}$), the pH at the equivalence point would have been lower than 7 because the acid is relatively stronger than the base.

Indicators

Acid–base titrations are carried out to establish the equivalent amounts of acid and base that react with each other, and hence the concentration of the acid or the alkali. We need some way of determining when equivalent amounts of acid and base have been mixed, and this can be done either using a pH meter and looking for the point of inflexion in the titration curve or, more usually and more conveniently, by using an acid–base indicator.

Indicators are either weak acids or weak bases. First, we consider an indicator that is a weak acid, represented by HIn. The indicator dissociates according to the equation:

$$\textbf{HIn}(aq) \rightleftharpoons H^+(aq) + \textbf{In}^-(aq)$$
colour I   **colour II**
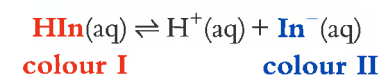
The ionised (**In**⁻) and un-ionised (**HIn**) forms must have different colours for the substance to function as an indicator. In this case, we will take the colours as **red** and **blue**, as shown in the equation.

If we add some indicator to a solution and the colour of the indicator is blue, this indicates that the position of the above equilibrium lies mostly to the right – there is so much more of the blue form than the red form that the solution appears blue to our eyes.

If we now add some acid to the solution, the colour of the indicator changes to red (Figure **8.26**). This can be understood in terms of Le Chatelier's principle. If acid (H^+) is added to the system at equilibrium, the position of equilibrium will shift to the left to use up, as far as possible, the H^+ that has been added. As the position of equilibrium shifts to the left, there is now significantly more HIn (red) than In⁻ (blue) and the colour of the indicator appears red.

If we now add some base to this solution, the colour changes to blue (Figure **8.27**). When we add some base, the OH⁻ ions from the base react with the H^+ ions on the right-hand side of the equilibrium to produce water. The position of equilibrium shifts to the right to replace the H^+ as far as possible and restore the value of K_c.

If we now consider an indicator that is a weak base, this will be present in solution as, for example, the sodium salt, NaIn. The equilibrium in solution will be:

$$\textbf{In}^-(aq) + H_2O(l) \rightleftharpoons \textbf{HIn}(aq) + OH^-(aq)$$
colour I   **colour II**
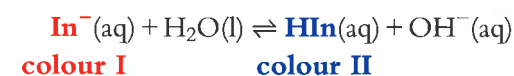
> The equivalence point is the **point of inflexion** on the curve. A point of inflexion is where the gradient (slope) of the curve stops increasing (or decreasing) and starts decreasing (or increasing).

> The equivalence point of a titration is the point at which equivalent numbers of moles of acid and alkali have been added. The **end point of a titration** is the point at which the indicator changes colour – these are not necessarily the same.

> Both colours are present, but we see the solution as if only one colour were present. Scientific reality is different to our everyday reality.
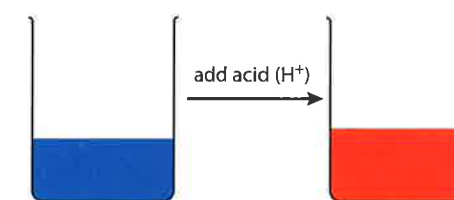
Figure 8.26 The indicator changes from colour II to colour I as acid is added.
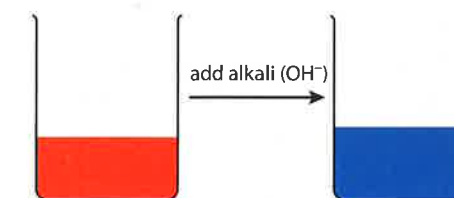
Figure 8.27 The indicator changes colour from colour I to colour II as alkali is added.

When some base (OH^-) is added, the position of equilibrium will shift to the left and the indicator will appear as colour I. If some acid is added it will react with the OH^- ions causing the position of equilibrium to shift to the right, so that the indicator appears to have colour II.

The pH range of an indicator

If we imagine a different indicator, for which the colours of the un-ionised and ionised forms are yellow and blue, respectively:
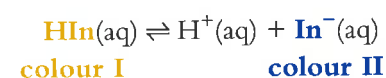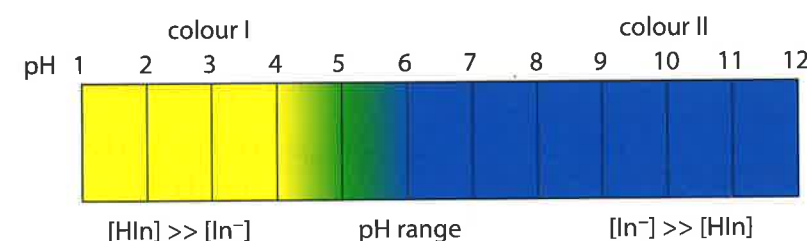
$$HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$$
$$\text{colour I} \qquad\qquad \text{colour II}$$

Let us consider increasing the pH gradually from 1. We could get the results for the colour of the indicator shown in Figure 8.28.

Figure 8.28 The variation of colour with pH for an indicator that is yellow in acidic solutions and blue in alkaline solution.

Up to pH 4 the concentration of HIn (yellow) is so much greater than the concentration of In^- (blue) that the indicator appears yellow. From pH 6 onwards, the concentration of In^- is so much greater than the concentration of HIn that the colour appears blue. Between pH 4 and 6 the concentrations of HIn and In^- are fairly evenly balanced, and the indicator is various shades of green in this region (green is a mixture of yellow and blue). In this region, if we gradually change the pH, we can see the indicator changing colour, and this is called the pH range of the indicator. In this case the pH range of the indicator would be quoted as 4–6.

The pH ranges of various indicators are given in Table 8.9.

Indicator	pH range	Acid colour	Alkali colour
methyl orange	3.1–4.4	red	yellow
bromophenol blue	2.9–4.6	yellow	blue
bromocresol green	3.8–5.4	yellow	blue
methyl red	4.2–6.3	red	yellow
bromothymol blue	6.0–7.6	yellow	blue
phenol red	6.8–8.4	yellow	red
phenolphthalein	8.2–10.0	colourless	pink

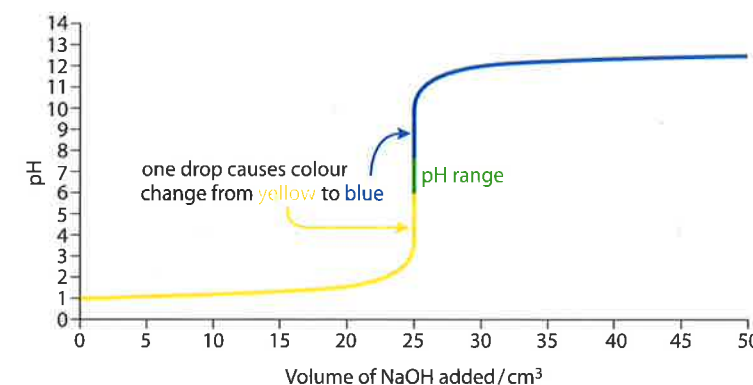**Table 8.9** The pH ranges and colours of some indicators.

Indicators can be made from natural substances – for example red cabbage and some types of flowers. Litmus is extracted from lichen.

The **pH range of an indicator is the pH values between which the indicator has intermediate colours because comparable amounts of the un-ionised and ionised forms are present.**

Universal indicator solution and pH paper contain a mixture of indicators that change colour over different pH ranges.

If an indicator is to be suitable for a titration, we require that one drop of the solution being added from the burette (either the acid or the base) should change the indicator from colour I to colour II. An indicator is no good for a titration if it can be seen to change colour gradually. Another way of saying this is that the indicator must be chosen to give a sharp end point. In order to have a clear end point for a titration, the range of the indicator must occur completely within the very steep part of the titration curve.

Consider a strong acid–strong base titration, as shown in Figure 8.29. In the vertical region of the curve, approximately one drop of alkali causes the pH to change by about 6–7 units. Therefore, if an indicator has its range in this part of the curve, adding one drop of alkali will cause the indicator to change from the acid colour to the alkali colour.

Where possible, an indicator should be chosen so that the equivalence point of the titration occurs within the pH range of the indicator.
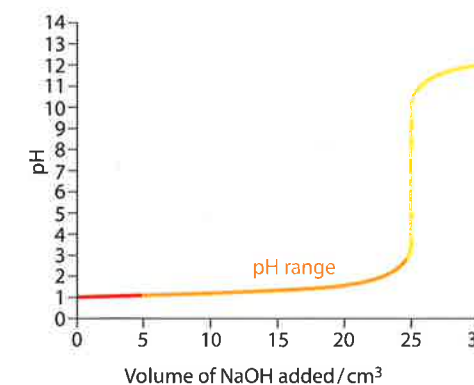

Figure 8.29 The colour changes of bromothymol blue during a strong acid–strong base titration.

Let us consider what happens if we use bromothymol blue for this titration. Before any base has been added, the colour of the indicator is yellow. As base is added, the colour remains yellow until the amount of base added is just less than $25.0\,cm^3$ and the pH of the mixture is about 4. At this point, adding one drop of base causes the pH to change from about 4 to 10 and the indicator changes colour from yellow to blue. So bromothymol blue is a suitable indicator for the titration because the pH range is entirely within the steep part of the titration curve and no intermediate colours are seen. We know that the equivalence point of the titration occurred somewhere within that one drop of base, and so we know the equivalence point to a good degree of precision.

If, we do the same titration with an indicator that changes colour from red to yellow and has a pH range of 1.2–2.8 we get the colour changes shown in Figure 8.30. The indicator is red in the acid solution, but as we add alkali we see the colour changing gradually from red, through orange to yellow. It has changed colour to yellow before the equivalence point and so we are not able to detect the equivalence point using this indicator.
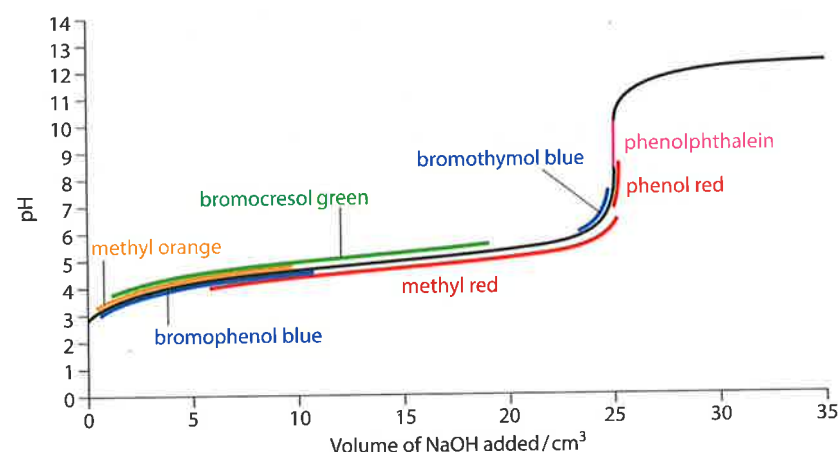
Depending on the concentrations of the solutions used, all the indicators in Table 8.9, are suitable for a strong acid–strong base titration.

Figure 8.30 The colour changes during a strong acid–strong base titration using an indicator with a pH range of 1.2–2.8.

**Figure 8.31** The ranges of various indicators superimposed on a weak acid–strong base titration curve.

Let us now consider a weak acid–strong base titration, as shown in Figure 8.31. The pH ranges of various indicators are shown on the curve for such as titration, and it can be seen that phenolphthalein is the most suitable indicator for this type of titration, with its pH range occurring entirely within the steep part of the curve. Phenol red is also suitable. Although bromothymol blue is not a suitable indicator for the titration shown, it may be suitable for other weak acid–strong base titrations.

For titrating a strong acid with a weak base, methyl red will generally be the most suitable indicator, but bromocresol green, methyl orange or bromophenol may also be suitable depending on the weak base used and the concentration of the acid.

Because the change in pH is gradual for titrating a weak acid with a weak base (no very steep part in the curve), it is not generally possible to carry out this titration with an indicator and obtain a good estimate of the equivalence point – it is difficult to judge the end point of the indicator; the indicator is seen to change colour gradually during the titration.

The pK_a value of an indicator

Consider the dissociation of an indicator that is a weak acid:
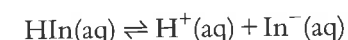
$$HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$$

The K_a expression for the indicator is:

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

At the midpoint of the pH range, half of the HIn will have dissociated and the concentrations of HIn and In$^-$ will be equal, in other words: $[HIn(aq)] = [In^-(aq)]$.

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

> **Because only strong acid–strong base titrations have pH = 7.0 at the end point, it is important to remember that the indicator is being used to determine the point at which equivalent numbers of moles of acid and alkali have been added, and not the point at which pH = 7.**

Taking $-\log_{10}$ of each side we get pK_a = pH. Therefore, the pK_a of the indicator is equal to the pH at the midpoint of its pH range. As a rough rule of thumb, we can take the pH range of an indicator to be p$K_a \pm 1$.

This is a theoretical derivation of the pH range of an indicator. In practice, due to our ability to detect various colours and colour changes, the midpoint of the working pH range of an indicator may not correspond exactly to the pK_a of the indicator.

We can now decide on the best indicator to use for a particular titration using the pK_a value for the indicator. The indicator will be suitable if its pK_a value is close to the pH at the equivalence point of the titration.

For an indicator that is a weak base, the pH range will be $(14 - pK_b) \pm 1$ and so an indicator will be suitable for a titration if $14 - pK_b$ is close to the pH at the equivalence point of the titration.

Titration using an indicator cannot be used to distinguish between a weak and a strong acid – if they have the same concentration, they will require the same amount of alkali to reach the equivalence point.

> pK_a for an indicator is sometimes given the symbol pK_{in}.

? Test yourself

32 Select a suitable indicator, from the list given, for each of the following titrations in which the alkali is added to 25.0 cm³ of acid.

phenolphthalein	pK_a = 9.3
bromocresol green	pK_a = 4.7
bromothymol blue	pK_a = 7.0

Acid	Alkali	Indicator
0.100 mol dm⁻³ CH₃COOH	0.100 mol dm⁻³ NaOH	
0.010 mol dm⁻³ HNO₃	0.020 mol dm⁻³ KOH	
0.010 mol dm⁻³ HCl	0.010 mol dm⁻³ NH₃	

33 Consider adding 0.0100 mol dm⁻³ sodium hydroxide solution to 25.0 cm³ of 0.0200 mol dm⁻³ ethanoic acid (pK_a = 4.76). Suggest values for the following important points on the titration curve.

initial pH	
volume of NaOH required to reach the equivalence point	
approximate pH at equivalence point	
approximate final pH (after approximately 200 cm³ of NaOH has been added)	

34 In the titration of 20.0 cm³ of a 0.100 mol dm⁻³ solution of a weak acid, HA, with 0.100 mol dm⁻³ sodium hydroxide solution, the pH when 10.0 cm³ of NaOH had been added was 4.80 and the pH when 20.0 cm³ of NaOH had been added was 8.80. What is the value of pK_a for HA?

- Work out whether a solution of a salt will have a pH of lower than, equal to or higher than 7
- Understand that the pH of a solution of a salt depends on the charge (and size) of the cation

Exam tip

One way of **thinking** about this is that the base is stronger than the acid, so the pH will be basic.

Remember – the weaker the acid, the stronger its conjugate base.

The reason given here is the same reason why the pH at the equivalence point in a weak acid–strong base titration is greater than 7.

pH meter

0.500 mol dm^{-3} ethanoate solution
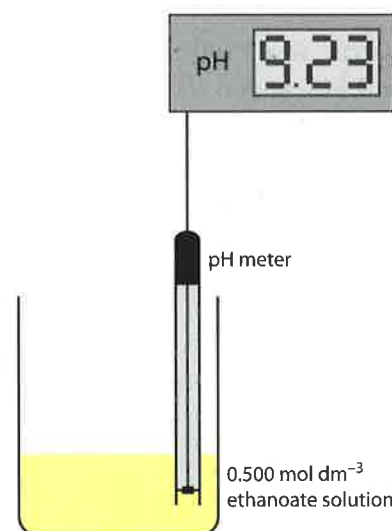
Figure 8.32 A solution of sodium ethanoate will have a pH > 7.

8.8.2 Salt hydrolysis

A salt will be formed when an acid reacts with a base:

$$\text{acid} + \text{base} \rightarrow \text{salt} + \text{water}$$

$$HNO_3 + NaOH \rightarrow NaNO_3 + H_2O$$
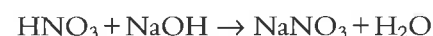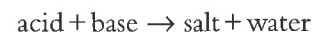
Sodium nitrate is the salt of a strong acid (HNO_3) and a strong base (NaOH).

When a solid salt is dissolved in water, the resulting solution may be acidic, basic or neutral, depending on the particular salt dissolving.

### Salt of a weak acid and a strong base (pH > 7)

Consider the salt sodium ethanoate ($CH_3COO^-Na^+$), formed when NaOH reacts with ethanoic acid (CH_3COOH):

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$
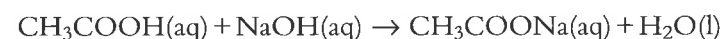
If some solid sodium ethanoate is dissolved in water, the pH of the solution will be greater than 7. A 0.500 mol dm^{-3} solution will have a pH of 9.23 (Figure **8.32**).

When the salt dissolves in water, the two ions separate from each other – the solution contains $CH_3COO^-(aq)$ and $Na^+(aq)$ ions.

The CH_3COO^- ion is the conjugate base of ethanoic acid (a weak acid) and so, acting as a base, will react with water molecules to accept a proton according to the equilibrium:

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$
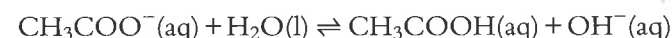
The concentration of OH^- ions in the solution has been increased and the solution is alkaline. This process is called **salt hydrolysis** – the salt has reacted with water.

The other ion from CH_3COONa present in this solution, the Na^+ ion, comes from a strong base (NaOH), which is fully ionised. There is therefore no tendency for Na^+ to react with the OH^- ions produced.

$$Na^+(aq) + OH^-(aq) \not\rightleftharpoons NaOH(aq)$$
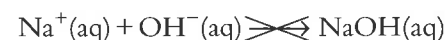
The pH of a 0.500 mol dm^{-3} solution of sodium ethanoate can be calculated as follows.

The pK_a of ethanoic acid is 4.76. pK_b for its conjugate base, the ethanoate ion, is given by:

$$pK_a + pK_b = pK_w$$

Therefore, at 25 °C, p$K_b = 14 - 4.76 = 9.24$. So K_b for the ethanoate ion is $10^{-9.24}$, or 5.75×10^{-10}.

The ethanoate ion reacts with water according to the equation:

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$
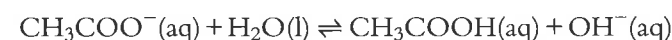
K_b for CH_3COO^- is:

$$K_b = \frac{[CH_3COOH(aq)][OH^-(aq)]}{[CH_3COO^-(aq)]}$$

One CH_3COO^- ion reacts with one H_2O molecule to form one molecule of CH_3COOH and one OH^- ion therefore:

$$[CH_3COOH(aq)] = [OH^-(aq)]$$

We will use the approximation that the extent to which the CH_3COO^- reacts is negligible compared with its concentration and take $[CH_3COO^-(aq)]$ to be 0.500 mol dm^{-3}.

Substituting known values into the K_b expression:

$$5.75 \times 10^{-10} = \frac{[OH^-(aq)]^2}{0.500}$$
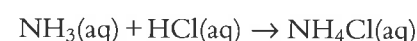
$$[OH^-] = 1.70 \times 10^{-5} \text{ mol dm}^{-3}$$

$$pOH = -\log_{10}[OH^-(aq)] = -\log_{10} 1.70 \times 10^{-5} = 4.77$$

$$pOH + pH = pK_w$$

At 25 °C, pOH + pH = 14, so pH = 14 − 4.77 = 9.23. Therefore the pH of a 0.500 mol dm^{-3} solution of sodium ethanoate is 9.23.

Salt of a strong acid and a weak base (pH < 7)

Consider ammonium chloride (NH_4Cl). This is the salt of a strong acid (HCl) and a weak base (NH_3):

$$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$$

When this is dissolved in water, an acidic solution is formed (Figure **8.33**).

The NH_4^+ is the conjugate acid of the weak base NH_3 and will therefore dissociate according to the equation:

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$$

H^+ is generated, and so the solution of NH_4Cl is acidic. The pH of a 0.500 mol dm^{-3} solution of NH_4Cl is 4.78.

Cl^- is the conjugate base of the strong acid, HCl. It is therefore an extremely weak base (the stronger the acid, the weaker the conjugate base). There is virtually no tendency for the following reaction to occur:

$$Cl^-(aq) + H_2O(l) \not\rightleftharpoons HCl(aq) + OH^-(aq)$$

The pH of a solution of ammonium chloride can be worked out using a similar method to that used to work out the pH of a sodium ethanoate solution above.

pH meter

0.500 mol dm^{-3} ammonium chloride solution
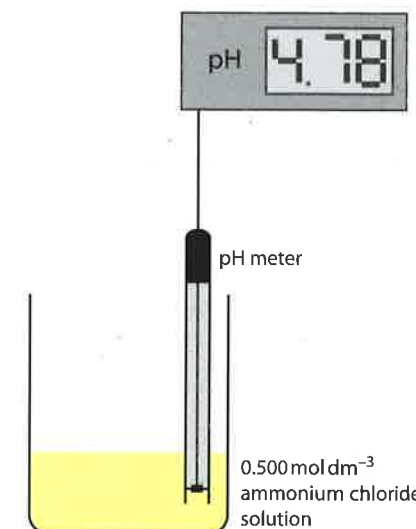
Figure 8.33 The pH of ammonium chloride solution is < 7.

Salt of a strong acid and a strong base (pH = 7)

Consider sodium chloride, NaCl. This is made from the strong acid HCl and the strong base NaOH. These are both fully dissociated in aqueous solution, so a solution of NaCl is neutral (pH 7 at 25 °C). There is virtually no tendency for either of these reactions to occur:

$$Na^+(aq) + OH^-(aq) \rightleftharpoons NaOH(aq)$$

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

Salt of a weak acid and a weak base (pH = ?)

Consider ammonium ethanoate $CH_3COO^-NH_4^+$. This is the salt of the weak acid (CH_3COOH) and the weak base ($NH_3(aq)$). It is not possible to predict whether the solution is acidic or alkaline without looking at the pK_a values.
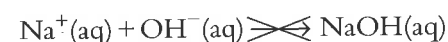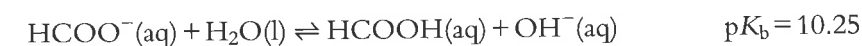
When ammonium ethanoate is dissolved in water, CH_3COO^- acts as a base and NH_4^+ acts as an acid:

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq) \qquad pK_b = 9.24$$

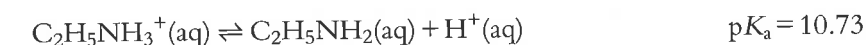$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq) \qquad pK_a = 9.25$$

Because the pK_b value is slightly lower (lower value = stronger) than the pK_a value, the solution will be slightly alkaline. However, the values are very close together, so the pH of a solution of ammonium ethanoate will be very close to 7.0.

A solution of ammonium methanoate would have a pH lower than 7:

$$HCOO^-(aq) + H_2O(l) \rightleftharpoons HCOOH(aq) + OH^-(aq) \qquad pK_b = 10.25$$

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq) \qquad pK_a = 9.25$$

because pK_a for the ammonium ion (stronger acid) is lower than pK_b for the methanoate ion.

A solution of ethylammonium ethanoate ($C_2H_5NH_3^+CH_3COO^-$) will have a pH higher than 7 because pK_b is lower (stronger base) than pK_a.

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq) \qquad pK_b = 9.24$$

$$C_2H_5NH_3^+(aq) \rightleftharpoons C_2H_5NH_2(aq) + H^+(aq) \qquad pK_a = 10.73$$

Acidity due to positive ions in solution

Let us consider a solution of iron(III) chloride. A $0.100\,mol\,dm^{-3}$ solution of iron(III) will have a pH of less than 2 (Figure **8.34**).

Positive ions in solution are hydrated to form aqueous ions, e.g. $Fe^{3+}(aq)$. The formula of $Fe^{3+}(aq)$ is $[Fe(H_2O)_6]^{3+}$. This ion dissociates in solution according to the equation:

$$[Fe(H_2O)_6]^{3+}(aq) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$$
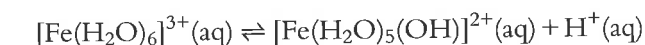
Hence the solution is acidic due to the H^+ ions produced.
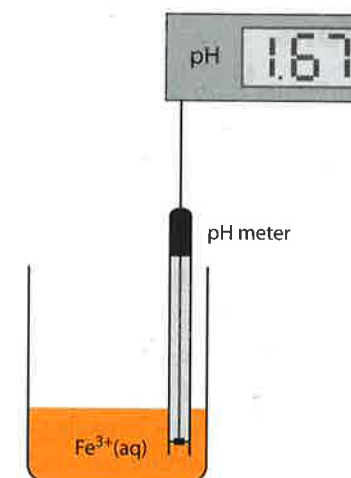

Figure 8.34 A solution containing 3+ ions has a pH < 7.

The reason that this occurs with 3+ ions is because of the high charge density (or charge to radius ratio) of the ion, which causes the water molecule to be sufficiently **polarised** for H^+ to dissociate. The Fe^{3+} ion pulls electrons away from the H_2O molecules, which increases the $\delta+$ charge on the hydrogen so that it is more readily lost as H^+ (Figure **8.35**).

The larger an ion is and the lower its charge, then the smaller the charge density of the ion and the lower its tendency to polarise water molecules. So the Fe^{2+} ion will cause less polarisation of water molecules and, although a solution of $Fe^{2+}(aq)$ will still be acidic, it will have a higher pH than a solution of $Fe^{3+}(aq)$ of the same concentration.
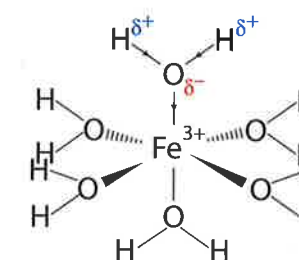
Figure 8.35 The polarisation of one of the water ligands in $[Fe(H_2O)_6]^{3+}$.

? Test yourself

35 Predict whether the pH of each of the following solutions will be equal to 7, greater than 7 or less than 7.

	pH
$0.100\,mol\,dm^{-3}$ $CH_3CH_2CH_2CH_2COONa$	
$0.500\,mol\,dm^{-3}$ KNO_3	
$0.100\,mol\,dm^{-3}$ Na_2CO_3	
$0.100\,mol\,dm^{-3}$ $CH_3CH_2NH_3^+Cl^-$	
$0.200\,mol\,dm^{-3}$ $CrCl_3$	

36 Calculate pH values for the following salt solutions:
   a a $0.100\,mol\,dm^{-3}$ solution of potassium cyanide (KCN), given that pK_a for hydrocyanic acid (HCN) is 9.40.
   b a $0.200\,mol\,dm^{-3}$ solution of sodium propanoate (CH_3CH_2COONa), given that the pK_a for propanoic acid is 4.87.

Learning objectives

- Understand what is meant by a buffer solution and how both acidic and basic buffers can be made
- Describe how a buffer solution works when small amounts of acid/base are added
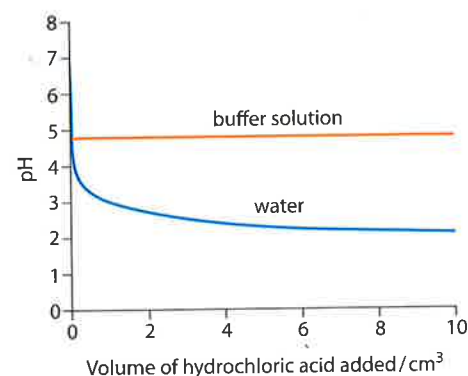
Figure 8.36 The pH of a buffer solution changes very little when hydrochloric acid is added. Water is not a good buffer.

The H$^+$ added is 'mopped up' by reaction with the ethanoate ion (a base).

The OH$^-$ added is 'mopped up' by reaction with the ethanoic acid.

8.8.3 Buffer solutions

The blue line on the graph in Figure **8.36** shows the result of adding 10 cm^3 of 0.100 mol dm^{-3} hydrochloric acid in stages to 100 cm^3 of water.

The orange line shows the effect of adding the hydrochloric acid to 100 cm^3 of a buffer solution formed by mixing 50 cm^3 of 1.00 mol dm^{-3} ethanoic acid and 50 cm^3 of 1.00 mol dm^{-3} sodium ethanoate. The pH of the water changes from 7.00 to 2.04 when 10 cm^3 of hydrochloric acid are added – the pH of the buffer solution changes from 4.76 to 4.74. When 10 cm^3 of 0.100 mol dm^{-3} sodium hydroxide are added to 100 cm^3 of the ethanoic acid/sodium ethanoate buffer solution, the pH changes from 4.76 to 4.78. The pH of the buffer solution remains virtually constant when an acid or a base is added, which leads to the definition of a **buffer solution**:

> a solution that resists changes in pH when small amounts of acid or alkali are added.

The 'small amount' in this definition is important. If, for instance, 33.3 cm^3 of 2.00 mol dm^{-3} hydrochloric acid is added to 100 cm^3 of the ethanoic acid/sodium ethanoate buffer solution we have just considered, the pH will change by about 4.5 units!

A buffer solution consists of two components and must always contain something to react with any acid added and something to react with any base added. In other words, a buffer solution always contains an acid and a base.

Buffers are important in many industrial processes and biological systems (for example, the blood – the pH of blood is about 7.4, and if it changes by about 0.5 in either direction you would die!). They are also used in products such as contact lens solutions, cosmetics and shampoos.

Acid buffer solutions

An acid buffer solution consists of a weak acid (e.g. ethanoic acid) and a salt of that weak acid (e.g. sodium ethanoate). The equilibrium in this solution is:

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

If some hydrochloric acid is added to this solution, the added H$^+$ reacts with the CH$_3$COO$^-$ in the solution:

$$CH_3COO^-(aq) + H^+(aq) \rightarrow CH_3COOH(aq)$$
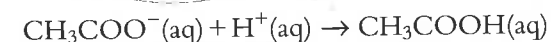
If some sodium hydroxide is added to the solution, the added OH$^-$ reacts with the CH$_3$COOH in the solution:

$$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$$
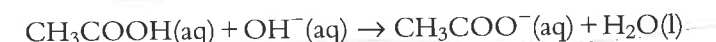
If we consider the expression for K_a we can understand why the pH changes so little:

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

This can be rearranged as:

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

Because K_a is a constant, this means that the H$^+$ concentration in the solution is proportional to the ratio of the ethanoic acid concentration to the ethanoate ion concentration.

For the solution to function as a buffer, both [CH$_3$COO$^-$(aq)] and [CH$_3$COOH(aq)] must be large so that any changes in their concentrations that occur when an acid or a base are added are small compared with these concentrations. This means that the value of the ratio ([CH$_3$COOH(aq)]:[CH$_3$COO$^-$(aq)]) changes very little and the [H$^+$(aq)] value (and pH) changes very little.

Let us consider a buffer solution in which the concentrations of ethanoic acid and sodium ethanoate are both 0.500 mol dm^{-3}. If we take 100.0 cm^3 of this solution, the number of moles of CH$_3$COOH and CH$_3$COO$^-$ are given by:

no. moles = concentration × volume (in dm^3)

no. moles of CH$_3$COOH = no. moles of CH$_3$COO$^-$

$$= 0.500 \times \frac{100.0}{1000} = 0.0500 \text{ mol}$$

If 1.00 cm^3 of 0.100 mol dm^{-3} HCl is added to this solution:

$$\text{no. moles of HCl} = 0.100 \times \frac{1.00}{1000} = 1.00 \times 10^{-4} \text{ mol}$$

The acid will react with the ethanoate ions:

	CH$_3$COO$^-$(aq) + H$^+$(aq) $\rightleftharpoons$ CH$_3$COOH(aq)	
initial no. moles / mol	0.0500	0.0500
no. moles after HCl added / mol	0.0500 − 1.00 × 10^{-4}	0.0500 + 1.00 × 10^{-4}
i.e.	0.0499	0.0501

The concentrations after the HCl has been added can be worked out by dividing the number of moles by the new volume (100 cm^3 + 1 cm^3 = 101 cm^3 = 0.101 dm^3)

	CH$_3$COO$^-$(aq) + H$^+$(aq) $\rightleftharpoons$ CH$_3$COOH(aq)	
concentration after HCl added / mol dm^{-3}	0.494	0.496

We can now, using Table **8.10**, compare the ratio [CH$_3$COOH(aq)] : [CH$_3$COO$^-$(aq)] before and after adding the HCl.

	$\dfrac{[CH_3COOH(aq)]}{[CH_3COO^-(aq)]}$	K_a	$\dfrac{[CH_3COOH(aq)]}{[CH_3COO^-(aq)]} \times K_a$	[H$^+$(aq)] / mol dm^{-3}	pH
Before adding HCl	1.000	1.738 × 10^{-5}	1.738 × 10^{-5}	1.738 × 10^{-5}	4.760
After adding HCl	1.004	1.738 × 10^{-5}	1.745 × 10^{-5}	1.745 × 10^{-5}	4.758

Table 8.10 Comparing the [acid] : [base] ratio in a buffer solution.

It can be seen that because the concentrations of both CH_3COOH and CH_3COO^- are large compared with the amount of acid added, the addition of a small amount of HCl hardly changes the $[CH_3COOH(aq)]$: $[CH_3COO^-(aq)]$ ratio at all, and, to three significant figures, the pH does not change.

If we do the same calculation but add the hydrochloric acid to a solution of $0.500\,mol\,dm^{-3}$ ethanoic acid (i.e. no ethanoate is originally present, but a small amount of ethanoate is formed from the dissociation of the acid):

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

|			
initial equilibrium concentration / $mol\,dm^{-3}$	0.497	2.94×10^{-3}	2.94×10^{-3}
concentration after HCl added / $mol\,dm^{-3}$	0.493	1.92×10^{-3}	

	$\dfrac{[CH_3COOH(aq)]}{[CH_3COO^-(aq)]}$	K_a	$\dfrac{[CH_3COOH(aq)]}{[CH_3COO^-(aq)]} \times K_a$	$[H^+(aq)]/mol\,dm^{-3}$	pH
Before adding HCl	169	1.738×10^{-5}	2.93×10^{-3}	2.93×10^{-3}	2.53
After adding HCl	257	1.738×10^{-5}	4.47×10^{-3}	4.47×10^{-3}	2.35

Table 8.11 Comparing the [acid]:[base] ratio in a non-buffer solution.

In this case, for the same addition of HCl, the pH has changed by almost 100 times as much (Table **8.11**). This is because the initial concentration of the ethanoate ion was so small that any small change in concentration caused a significant percentage change in its concentration, and hence in the value of the ratio $[CH_3COOH(aq)]$: $[CH_3COO^-(aq)]$ and therefore in the pH.

Basic buffer solutions

A basic buffer solution consists of a weak base (e.g. ammonia) and a salt of that weak base (e.g. ammonium chloride). The equilibrium in this solution is:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
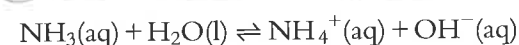
If some hydrochloric acid is added to this solution, the added H^+ reacts with the NH_3 in the solution:

$$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$$
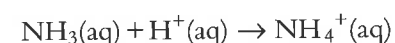
If some sodium hydroxide is added to the solution, the added OH^- reacts with the NH_4^+ in the solution:

$$NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(l)$$
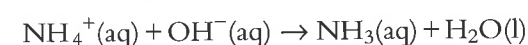
As above, if the concentrations of NH_3 and NH_4^+ in the solution are both high, any small change in their concentrations has very little effect on the $[NH_4^+(aq)]$: $[NH_3(aq)]$ ratio in the K_b expression.

$$K_b = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]}$$

The value of the OH^- concentration, and hence the pH, therefore changes very little.

The H^+ added is 'mopped up' by reaction with the ammonia.

The OH^- added is 'mopped up' by reaction with the ammonium ion.

Making buffer solutions by partial neutralisation of a weak acid/base

A buffer solution can be made by partial neutralisation of a weak acid with a strong base – for example by adding sodium hydroxide to ethanoic acid. The reaction that occurs is:

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O$$
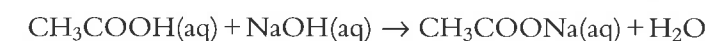
When $10\,cm^3$ of $0.100\,mol\,dm^{-3}$ NaOH is added to $25\,cm^3$ of $0.100\,mol\,dm^{-3}$ CH_3COOH, some of the ethanoic acid will be converted to sodium ethanoate, but there will still be some ethanoic acid left. So the solution contains both ethanoic acid and sodium ethanoate, which are the components of a buffer system. As long as the number of moles of sodium hydroxide added is fewer than the number of moles of ethanoic acid present in the original solution, the solution will contain both ethanoic acid and sodium ethanoate and act as a buffer.

The graph in Figure **8.37** shows the titration curve of a weak acid (ethanoic acid) with a strong base (NaOH). The shaded region in Figure **8.37** represents the pH range over which this solution acts as buffer. In this region, significant amounts of both ethanoic acid and sodium ethanoate are present and adding sodium hydroxide does not cause the pH to change very much; addition of $20\,cm^3$ of NaOH in this region causes the pH to change by only about 1.5 units. Although this seems to be a much more significant increase than we have seen above, it must be remembered that here we are adding sodium hydroxide of the same concentration as the ethanoic acid to a similar volume of solution – we are not just adding small amounts.

A buffer solution can be also be made by partial neutralisation of a weak base with a strong acid – for example when hydrochloric acid is added to ammonia solution. The reaction that occurs is:

$$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$$
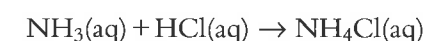
As long as the number of moles of hydrochloric acid added is lower than the number of moles of ammonia in the solution, the solution will contain some NH_3 and some NH_4Cl and will act as a buffer. The titration curve for adding $0.100\,mol\,dm^{-3}$ HCl to $25\,cm^3$ of $0.100\,mol\,dm^{-3}$ ammonia solution is shown in Figure **8.38** and the buffering region is marked.
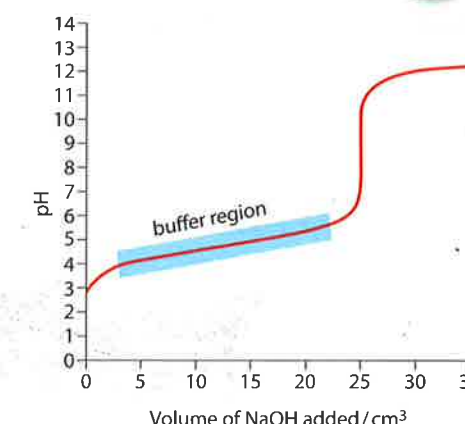
Figure 8.37 The buffering region in a weak acid–strong base titration curve.
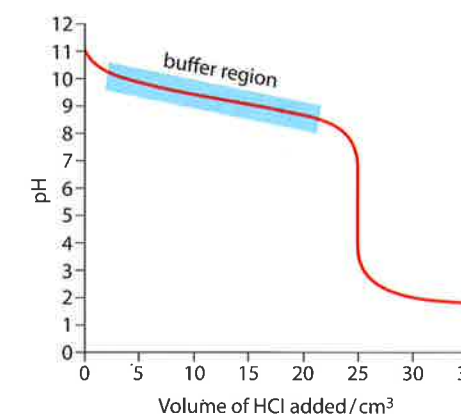
Figure 8.38 The buffering region in a strong acid–weak base titration curve.

? **Test yourself**

37 State whether or not each of the following mixtures would constitute a buffer solution:
a $50\,cm^3$ $0.100\,mol\,dm^{-3}$ $CH_3CH_2COOH(aq)$ and $25\,cm^3$ $0.100\,mol\,dm^{-3}$ $CH_3CH_2COONa(aq)$
b $50\,cm^3$ $0.100\,mol\,dm^{-3}$ $CH_3CH_2COOH(aq)$ and $25\,cm^3$ $0.100\,mol\,dm^{-3}$ $HCOONa(aq)$
c $50\,cm^3$ $0.100\,mol\,dm^{-3}$ $HCOOH(aq)$ and $75\,cm^3$ $0.100\,mol\,dm^{-3}$ $HCOONa(aq)$
d $25\,cm^3$ $0.010\,mol\,dm^{-3}$ $NaOH(aq)$ and $25\,cm^3$ $0.020\,mol\,dm^{-3}$ $CH_3COOH(aq)$
e $50\,cm^3$ $0.200\,mol\,dm^{-3}$ $HCl(aq)$ and $25\,cm^3$ $0.400\,mol\,dm^{-3}$ $NaCl(aq)$
f $50\,cm^3$ $0.100\,mol\,dm^{-3}$ $NH_3(aq)$ and $50\,cm^3$ $0.100\,mol\,dm^{-3}$ $NH_4NO_3(aq)$
g $50\,cm^3$ $0.100\,mol\,dm^{-3}$ $NH_3(aq)$ and $25\,cm^3$ $0.100\,mol\,dm^{-3}$ $HCl(aq)$

Exam-style questions

1 Consider the dissociation of carbonic acid in aqueous solution:

$$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+ \qquad \textbf{reaction 1}$$
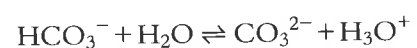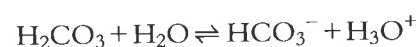
$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+ \qquad \textbf{reaction 2}$$

Which of the following is correct?

A HCO_3^- acts as an acid in reaction 1 but as a base in reaction 2.
B HCO_3^- is the conjugate base of H_2O.
C HCO_3^- is the conjugate acid of CO_3^{2-}.
D H_2CO_3 and CO_3^{2-} are a conjugate acid–base pair.

2 The pH of a solution of $0.0100\,mol\,dm^{-3}$ hydrochloric acid is 2. A $10\,cm^3$ sample of the acid is measured out and distilled water added to dilute it to a total volume of $100\,cm^3$. How do the hydrogen ion concentration and the pH change as this solution is diluted?

	hydrogen ion concentration	pH
A	decreases by a factor of 10	increases by 1
B	decreases by a factor of 100	decreases by 2
C	increases by a factor of 10	increases by 1
D	decreases by a factor of 10	decreases by 1

3 The electrical conductivity of five aqueous solutions is measured:

I $0.100\,mol\,dm^{-3}$ $NaOH(aq)$
II $0.100\,mol\,dm^{-3}$ $CH_3COOH(aq)$
III $0.100\,mol\,dm^{-3}$ $NH_4Cl(aq)$
IV $0.100\,mol\,dm^{-3}$ $NH_3(aq)$
V $0.100\,mol\,dm^{-3}$ $HCl(aq)$

Which of the following is correct?

A The conductivity of **I** is higher than that of **II** but lower than that of **IV**.
B The conductivity of **III** is higher than that of **II** and higher than that of **IV**.
C The conductivity of **V** is lower than that of **II** but higher than that of **III**.
D The conductivity of **I** is lower than that of **III** and lower than that of **IV**.

4 HCN is a weak acid and dissociates in water according to the following equilibrium:

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$$
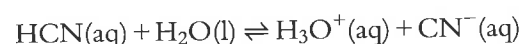
Which of the following statements is correct?

A HCN dissociates completely in solution.
B The concentration of CN^- ions is greater than that of HCN.
C CN^- is a stronger base than H_2O.
D H_3O^+ acts as a Brønsted–Lowry base.

5 What is the pH of a $1.00 \times 10^{-5}\,mol\,dm^{-3}$ solution of sodium hydroxide?

A 5   **B** 9   **C** 13   **D** 14

HL 6 The acid HA has a K_a value of 1.00×10^{-7}. What is the pH of a $0.100\,mol\,dm^{-3}$ solution of HA?

A 7   **B** 4   **C** 8   **D** 3

HL 7 The following salts are dissolved in water:

I $NaCl$ **III** Na_2CO_3
II CH_3COONa **IV** $FeCl_3$

Which of these solutions will have a pH higher than 7?

A **I** and **IV** only   **C** **IV** only
B **II** and **III** only   **D** **II** only

HL 8 A series of solutions are made up:

I $50\,cm^3$ $0.100\,mol\,dm^{-3}$ CH_3COOH and $25\,cm^3$ $0.100\,mol\,dm^{-3}$ $NaOH$
II $50\,cm^3$ $0.050\,mol\,dm^{-3}$ CH_3COOH and $25\,cm^3$ $0.100\,mol\,dm^{-3}$ $NaOH$
III $25\,cm^3$ $0.100\,mol\,dm^{-3}$ CH_3COOH and $50\,cm^3$ $0.100\,mol\,dm^{-3}$ $NaOH$
IV $25\,cm^3$ $0.100\,mol\,dm^{-3}$ CH_3COOH and $50\,cm^3$ $0.100\,mol\,dm^{-3}$ CH_3COONa

Which solution(s) is/are buffer solutions?

A **I** and **IV** only
B **III** and **IV** only
C **II**, **III** and **IV** only
D **I** and **II** only

HL 9 The pK_a values for four indicators are shown here.

Indicator	pK_a
methyl violet	0.8
bromocresol green	4.7
phenol red	7.9
phenolphthalein	9.3

Which indicator would be most suitable for a titration in which $0.0100\,mol\,dm^{-3}$ ammonia is added gradually to $25.00\,cm^3$ of $0.0100\,mol\,dm^{-3}$ hydrochloric acid?

A methyl violet
B bromocresol green
C phenol red
D phenolphthalein

HL 10 According to the Lewis definition, an acid is:

    A a proton donor

    B an electron pair donor

    C an electron acceptor

    D an electron pair acceptor

11 Ethanoic acid is a weak acid and hydrochloric acid is a strong acid.

  a Write an equation for the reaction of ethanoic acid with water, and identify the conjugate base of ethanoic acid. **[2]**

  b Explain the difference between a strong acid and a weak acid. **[2]**

  c **i** Calculate the pH of a $1.00 \times 10^{-3}\,\text{mol dm}^{-3}$ solution of hydrochloric acid.

      ii Suggest a value for the pH of a $1.00 \times 10^{-3}\,\text{mol dm}^{-3}$ solution of ethanoic acid. **[3]**

  d One method for distinguishing between a strong and a weak acid involves reacting them with a metal such as magnesium.

     i Write an equation for the reaction between magnesium and ethanoic acid and name the products of the reaction. **[2]**

     ii Explain how this method enables a strong acid to be distinguished from a weak acid. **[2]**

12 Water ionises slightly and the value of the ionic product constant at 298 K is 1.0×10^{-14}.

  a Write an equation for the ionisation of water. **[1]**

  b Write an expression for the ionic product constant for water. **[1]**

  c Calculate the pH of a $0.10\,\text{mol dm}^{-3}$ solution of sodium hydroxide at 298 K. **[3]**

  d Explain whether a $0.10\,\text{mol dm}^{-3}$ solution of barium hydroxide will have a higher or lower pH than a $0.10\,\text{mol dm}^{-3}$ solution of sodium hydroxide at the same temperature. **[2]**

HL 13 **a** Define pH. **[1]**

  b The pK_a value of butanoic acid is 4.82. Determine the pH of a $0.150\,\text{mol dm}^{-3}$ solution of butanoic acid. **[4]**

  c Explain, using a chemical equation, whether the pH of a $0.100\,\text{mol dm}^{-3}$ solution of sodium butanoate will be lower than 7, higher than 7 or equal to 7. **[3]**

  d $25.00\,\text{cm}^3$ of $0.150\,\text{mol dm}^{-3}$ butanoic acid is titrated with sodium hydroxide solution. $27.60\,\text{cm}^3$ of sodium hydroxide is required to reach the equivalence point.

     i Calculate the concentration of the sodium hydroxide solution. **[3]**

     ii Calculate the pH of the sodium hydroxide solution. **[3]**

     iii Sketch a graph to show how the pH changes as the sodium hydroxide is added to the butanoic acid up to a total volume of $50\,\text{cm}^3$ of sodium hydroxide. **[3]**

     iv Suggest, with a reason, a suitable indicator for the titration. **[2]**

HL 14 Propanoic acid has a pK_a of 4.87 and ethanoic acid has a pK_a of 4.76.

  a Write an equation for the ionisation of propanoic acid in water. **[2]**

  b Calculate the values of K_a for propanoic acid and ethanoic acid and use them to explain which is the stronger acid. **[4]**

  c Calculate the concentration of H^+ ions and pH of a $0.250\,\text{mol dm}^{-3}$ solution of propanoic acid, stating any assumptions you make. **[4]**

  d Write an equation for the reaction of the propanoate ion ($CH_3CH_2COO^-$) with water. **[1]**

  e Calculate the value of K_b for the propanoate ion. **[2]**

  f Calculate the pOH and pH of a $0.200\,\text{mol dm}^{-3}$ solution of sodium propanoate. **[4]**

HL 15 The value of the ionic product constant for water, K_w, is 5.48×10^{-14} at 323 K.

  a Write an equation for the ionisation of water. **[1]**

  b Calculate the pH of water at 323 K. **[3]**

  c A solution has a pOH of 7.0 at 323 K. State and explain whether this solution is acidic, alkaline or neutral. **[3]**

  d pK_w for water is 14.34 at 288 K. Explain whether the ionisation of water is exothermic or endothermic. **[3]**

HL 16 A buffer solution can be made by mixing together ammonia solution and ammonium chloride solution. The pK_b of ammonia is 4.75.

  a State what is meant by a buffer solution. **[2]**

  b Explain, using equations, what happens when sodium hydroxide and hydrochloric acid are added separately to separate samples of this buffer solution. **[2]**

  c Calculate the pOH of $25.0\,\text{cm}^3$ of a $0.125\,\text{mol dm}^{-3}$ solution of ammonia. **[3]**

  d A buffer solution can also be made by adding hydrochloric acid to the solution in part **c**. State and explain the value of the pH of the buffer when $12.5\,\text{cm}^3$ of $0.125\,\text{mol dm}^{-3}$ hydrochloric acid have been added to the solution in part **c**. **[3]**

Summary

A base must have a lone pair of electrons; an acid must have space in the outer shell to accept a lone pair. — **Lewis:**
– an ACid is an electron pair ACceptor
– a base is an electron pair donor

Brønsted–Lowry:
– an acid is a proton (H^+) donor
– a base is a proton acceptor

definitions

reactions

alkali + acid → salt + H_2O

base + acid → salt + H_2O

acid + carbonate/hydrogencarbonate → salt + CO_2 + H_2O

metal + acid → salt + H_2

examples: HCl, H_2SO_4 (first dissociation only), HNO_3

examples: group 1 hydroxides, $Ba(OH)_2$

Strong acids dissociate completely in aqueous solution.

Strong bases ionise completely in aqueous solution.

| pH < 7 acidic | pH = 7 neutral | pH > 7 basic |

pH $= -\log_{10}[H^+]$ —— no units

If $[H^+]$ decreases by a factor of 10, the pH increases by 1.

strong and weak acids and bases

ACIDS AND BASES

distinguishing between strong and weak acids experimentally

Weak acids dissociate only partially in aqueous solution.

Weak bases ionise only partially in aqueous solution.

examples: carboxylic acids (such as CH_3COOH) and H_2CO_3

examples: NH_3 and amines

at equal concentration

strong acids conduct electricity better

strong acids have lower pH

strong acids react more violently with metals or carbonates

To TITRATION, SALT HYDROLYSIS and BUFFER SOLUTION on the next page

ionic product constant for water
$K_w = [H^+(aq)][OH^-(aq)]$
$= 1.0 \times 10^{-14}$ at 25 °C

refers to $H_2O \rightleftharpoons H^+ + OH^-$ for any aqueous solution

$pH + pOH = pK_w$

for pure water: $pH = pOH = \dfrac{pK_w}{2}$

Stronger acids have higher K_a.

acid dissociation constant
$K_a = \dfrac{[A^-][H^+]}{[HA]}$
for $HA \rightleftharpoons H^+ + A^-$

$pH = \frac{1}{2}(pK_a - \log_{10}[\text{acid}])$

$K_w = K_a \times K_b$
and
$pK_w = pK_a + pK_b$
for a conjugate acid–base pair

Stronger bases have higher K_b.

base ionisation constant
$K_b = \dfrac{[BH^+][OH^-]}{[B]}$
for $B + H_2O \rightleftharpoons BH^+ + OH^-$

$pOH = \frac{1}{2}(pK_b - \log_{10}[\text{base}])$

TITRATION —— A **titration curve** (pH curve) shows how the pH varies in the titration of an acid with a base, or vice versa.

indicator: a weak acid or weak base in which the ionised and un-ionised forms have different colours

equivalence point: point at which equivalent amounts of acid and alkali have been added

At this point on a titration curve, the gradient stops decreasing and starts increasing, or vice versa.

acid	base	pH at equivalence point
strong	strong	7
strong	weak	<7
weak	strong	>7
weak	weak	?

$HIn \rightleftharpoons H^+ + In^-$
colour 1   colour 2

If acid is added, the equilibrium shifts towards the un-ionised form (colour 1).

$pH = pK_a$ at half-equivalence point

pH range of an indicator: range in which intermediate colours are seen

The indicator should be chosen so that its pH range lies within the steep part of the titration curve.

$pOH = pK_b$ at half-equivalence point

SALT HYDROLYSIS —— A salt dissolves in water to produce a solution that is acidic, basic or neutral, depending on the strengths of the acid and base used to make the salt.

3+ ions polarise H_2O molecules sufficiently for them to dissociate, therefore they produce an acidic solution.

acid	base	pH of solution	example
strong	strong	7	NaCl
strong	weak	<7	NH_4Cl
weak	strong	>7	CH_3COONa
weak	weak	?	CH_3COONH_4

BUFFER SOLUTION —— made using a weak acid and its salt or a weak base and its salt

solution that resists changes in pH when **small** amounts of acid or base are added

CH_3COOH/CH_3COONa

NH_3/NH_4Cl

add acid
$CH_3COO^- + H^+ \rightarrow CH_3COOH$

add base
$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$

add acid
$NH_3 + H^+ \rightarrow NH_4^+$

add base
$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$