08

Acids and bases

Essential ideas

8.1 Many reactions involve the transfer of a proton from an acid to a base.

8.2 The characterization of an acid depends on empirical evidence such as the production of gases in reactions with metals, the colour changes of indicators, or the release of heat in reactions with metal oxides and hydroxides.

8.3 The pH scale is an artificial scale used to distinguish between acid, neutral, and basic/alkaline solutions.

8.4 The pH depends on the concentration of the solution. The strength of acids or bases depends on the extent to which they dissociate in aqueous solution.

18.1 The acid–base concept can be extended to reactions that do not involve proton transfer.

18.2 The equilibrium law can be applied to acid–base reactions. Numerical problems can be simplified by making assumptions about the relative concentrations of the species involved. The use of logarithms is also significant here.

18.3 pH curves can be investigated experimentally but are mathematically determined by the dissociation constants of the acid and base. An indicator with an appropriate end point can be used to determine the equivalence point of the reaction.

8.5 Increased industrialization has led to greater production of nitrogen and sulfur oxides leading to acid rain, which is damaging our environment. These problems can be reduced through collaboration with national and intergovernmental organizations.

Acid–base theory informs much of our research into rainwater pollution and other aspects of environmental change.

The burning feeling of acid indigestion, the sour taste of grapefruit, and the vinegary smell of wine that has been exposed to the air are just some of the everyday encounters we have with acids. Likewise alkalis, or bases, are familiar substances – for example in baking soda, in household cleaners that contain ammonia, and in medication against indigestion. So what are the defining properties of these two groups of substances?

This question has intrigued chemists for centuries. The word 'acid' is derived from the Latin word *acetum* meaning sour – early tests to determine whether a substance was acidic were based on tasting! But it was learned that acids had other properties in common too: for example they changed the colour of the dye litmus from blue to red and they corroded metals. Similarly, alkalis were known to have distinctive properties such as being slippery to the touch, being able to remove fats and oils from fabrics, and turning litmus from red to blue. The name alkali comes from the Arabic word for plant ash, *alkalja*, where they were first identified. Early theories about acids and alkalis focused only on how they reacted together – it was actually suggested that the sourness of acids came from their possession of sharp angular spikes which became embedded in soft, rounded particles of alkali!

Over the last 120 years, our interpretation of acid–base behaviour has evolved alongside an increasing knowledge of atomic structure and bonding. In this chapter, we explore the modern definitions of acids and bases and learn how these help us to interpret and predict their interactions. Acid–base theory is central to topics such as air and water pollution, how global warming may affect the chemistry of the oceans, the action of drugs in the body, and many other aspects of cutting-edge research. As most acid–base reactions involve equilibria, much of the approach and mathematical content is based on work covered in Chapter 7. It is strongly recommended that you are familiar with this work before starting this chapter.

◀ A food scientist testing a sample of a batch of orange juice in a factory in France. pH measurements are an important part of the quality control of the product.

8.1 Theories of acids and bases

Understandings:
- A Brønsted–Lowry acid is a proton/H$^+$ donor and a Brønsted–Lowry base is a proton/H$^+$ acceptor.
  Guidance
  Students should know the representation of a proton in aqueous solution as both H$^+$(aq) and H$_3$O$^+$(aq).
- Amphiprotic species can act as both Brønsted–Lowry acids and bases.
- A pair of species differing by a single proton is called a conjugate acid–base pair.

Applications and skills:
- Deduction of the Brønsted–Lowry acid and base in a chemical reaction.
  Guidance
  The location of the proton transferred should be clearly indicated. For example, CH$_3$COOH/CH$_3$COO–rather than C$_2$H$_4$O$_2$/C$_2$H$_3$O$_2^-$.
- Deduction of the conjugate acid or conjugate base in a chemical reaction.
  Guidance
  Lewis theory is not required here.

Early theories

The famous French chemist Lavoisier proposed in 1777 that oxygen was the 'universal acidifying principle'. He believed that an acid could be defined as a compound of oxygen and a non-metal. In fact, the name he gave to the newly discovered gas *oxygen* means 'acid-former'. This theory, however, had to be dismissed when the acid HCl was proven to be made of hydrogen and chlorine only – no oxygen. To hold true, of course, any definition of an acid has to be valid for *all* acids.

A big step forward came in 1887 when the Swedish chemist Arrhenius suggested that an acid could be defined as a substance that dissociates in water to form hydrogen ions (H^+) and anions, while a base dissociates into hydroxide (OH^-) ions and cations. He also recognized that the hydrogen and hydroxide ions could form water, and the cations and anions form a salt. In a sense, Arrhenius was very close to the theory that is widely used to explain acid and base properties today, but his focus was only on aqueous systems. A broader theory was needed to account for reactions occurring without water, and especially for the fact that some insoluble substances show base properties.

> Svante August Arrhenius (1859–1927) wrote up his ideas on acids dissociating into ions in water as part of his doctoral thesis while a student at Stockholm University. But his theory was not well received and he was awarded the lowest possible class of degree. Later, his work gradually gained recognition and he received one of the earliest Nobel Prizes in Chemistry in 1903.
>
> Arrhenius may be less well known as the first person documented to predict the possibility of global warming as a result of human activity. In 1896, aware of the rising levels of CO_2 caused by increased industrialization, he calculated the likely effect of this on the temperature of the Earth. Today, over 100 years later, the significance of this relationship between increasing CO_2 and global temperatures has become a subject of major international concern.

Brønsted–Lowry: a theory of proton transfer

In 1923 two chemists, Martin Lowry of Cambridge, England, and Johannes Brønsted of Copenhagen, Denmark, working independently, published similar conclusions regarding the definitions of acids and bases. Their findings overcame the limitations of Arrhenius' work and have become established as the **Brønsted–Lowry theory**.

This theory focuses on the transfer of H^+ ions during an acid–base reaction: acids donate H^+ while bases accept H^+. For example, in the reaction between HCl and NH_3:

$$HCl + NH_3 \rightleftharpoons NH_4^+ + Cl^-$$
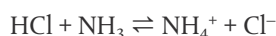
HCl transfers H^+ to NH_3 and so acts as an acid; NH_3 accepts the H^+ and so acts as a base.
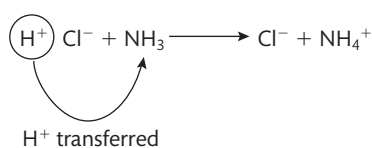
Figure 8.1 HCl transfers H^+ to NH_3.

Hydrogen atoms contain just one proton and one electron, so when they ionize by losing the electron, all that is left is the proton. Therefore *H^+ is equivalent to a proton,* and we will use the two terms interchangeably here.

The Brønsted–Lowry theory can therefore be stated as:

• a Brønsted–Lowry acid is a proton (H^+) donor;
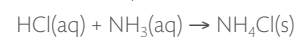• a Brønsted–Lowry base is a proton (H^+) acceptor.

Reaction between vapours of HCl and NH_3 forming the white smoke of ammonium chloride NH_4Cl.
$$HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(s)$$

Brønsted and Lowry's work on acid–base theory may be a good example of what is sometimes referred to as 'multiple independent discovery'. This refers to cases where similar discoveries are made by scientists at almost the same time, even though they have worked independently from each other. Examples include the independent discovery of the calculus by Newton and Leibniz, the formulation of the mechanism for biological evolution by Darwin and Wallace, and derivation of the pressure–volume relationships of gases by Boyle and Mariotte. Nobel Prizes in Chemistry are commonly awarded to more than one person working in the same field, who may have made the same discovery independently. Multiple independent discoveries are likely increasing as a result of communication technology, which enables scientists who may be widely separated geographically to have access to a common body of knowledge as the basis for their research.

When a discovery is made by more than one scientist at about the same time, ethical questions can arise, such as whether the credit belongs to one individual or should be shared, and whether there are issues regarding intellectual property and patent rights. Historically, these issues have been settled in very different ways in different cases. Nonetheless, the peer review process in science aims to ensure that credit is correctly awarded to the scientist or scientists responsible for a discovery, and that published work represents a new contribution to work in that field.

## Conjugate pairs

A Brønsted–Lowry acid is a proton (H^+) donor.

A Brønsted–Lowry base is a proton (H^+) acceptor.

The act of donating cannot happen in isolation – there must always be something present to play the role of acceptor. In Brønsted–Lowry theory, an acid can therefore only behave as a proton donor if there is also a base present to accept the proton.

Let's consider the acid–base reaction between a generic acid HA and base B:

$$HA + B \rightleftharpoons A^- + BH^+$$
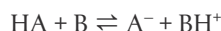
We can see that HA acts as an acid, donating a proton to B while B acts as a base, accepting the proton from HA. But if we look also at the reverse reaction, we can pick out another acid–base reaction: here BH^+ is acting as an acid, donating its proton to A^- while A^- acts as a base accepting the proton from BH^+. In other words acid HA has reacted to form the base A^-, while base B has reacted to form acid BH^+.

conjugate acid–base pair

$$HA + B \rightleftharpoons A^- + BH^+$$

conjugate acid–base pair
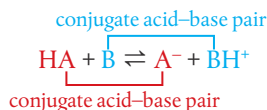
Acids react to form bases and vice versa. The acid–base pairs related to each other in this way are called **conjugate acid–base pairs**, and you can see that they *differ by just one proton*. It is important to be able to recognize these pairs in a Brønsted–Lowry acid–base reaction.

One example of a conjugate pair is H_2O and H_3O^+, which is found in all acid–base reactions in aqueous solution. The reaction

$$H_2O(l) + H^+(aq) \rightleftharpoons H_3O^+(aq)$$
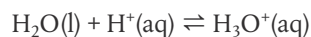
occurs when a proton released from an acid readily associates with H_2O molecules forming H_3O^+. In other words, protons become hydrated. H_3O^+ is variously called the hydroxonium ion, the oxonium ion, or the hydronium ion and is always the form of hydrogen ions in aqueous solution. However, for most reactions it is convenient simply to write it as $H^+(aq)$. Note that in this pair H_3O^+ is the conjugate acid and H_2O its conjugate base.

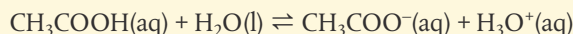Note that $H_3O^+(aq)$ and $H^+(aq)$ are both used to represent a proton in aqueous solution.

Lowry described the ready hydration of the proton as 'the extreme reluctance of the hydrogen nucleus to lead an isolated existence'.
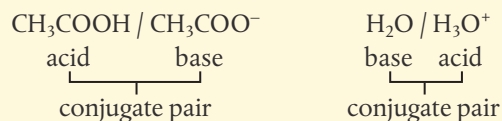
Worked example

Label the conjugate acid–base pairs in the following reaction:

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

Solution

$$CH_3COOH \,/\, CH_3COO^-$$
acid   base

$$H_2O \,/\, H_3O^+$$
base   acid

conjugate pair   conjugate pair

The fact that in a conjugate pair the acid always has one proton more than its conjugate base, makes it easy to predict the formula of the corresponding conjugate for any given acid or base.
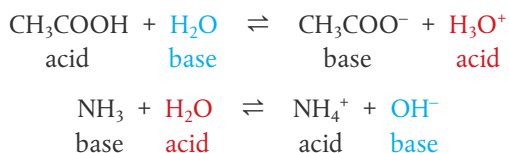
Worked example

1 Write the conjugate base for each of the following.

(a) H_3O^+ (b) NH_3 (c) H_2CO_3

2 Write the conjugate acid for each of the following.

(a) NO_2^- (b) OH^- (c) CO_3^{2-}

Solution

1 To form the base from these species, remove one H^+

(a) H_2O (b) NH_2^- (c) HCO_3^-

2 To form the acid from these species, add one H^+

(a) HNO_2 (b) H_2O (c) HCO_3^-

Some species can act as acids and as bases

You may be surprised to see water described in the answers to the Worked examples above as a base (Q1, part a), and as an acid (Q2, part b), as you are probably not used to thinking of water as an acid, or as a base, but rather as a neutral substance. The point is that Brønsted–Lowry theory describes acids and bases in terms of how they react together, so it all depends on what water is reacting with. Consider the following:

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$
acid   base   base   acid

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
base   acid   acid   base

So with CH_3COOH, water acts as a Brønsted–Lowry base, but with NH_3 it acts as a Brønsted–Lowry acid.

Notice that water is not the only species that can act as both an acid and a base – for example, we see in the Worked example below that HCO_3^- behaves similarly. Substances which can act as Brønsted–Lowry acids and bases in this way are said to be **amphiprotic**. What are the features that enable these species to have this 'double identity'?

When writing the conjugate acid of a base, add one H^+; when writing the conjugate base of an acid, remove one H^+. Remember to adjust the charge by the 1+ removed or added.

The acid and base in a conjugate acid–base pair differ by just one proton.

Amphoteros is a Greek word meaning 'both'. For example amphibians are adapted both to water and to land.

An amphiprotic substance is one which can act as both a proton donor and a proton acceptor.

To act as a Brønsted–Lowry acid, they must be able to dissociate and release H^+.

To act as a Brønsted–Lowry base, they must be able to accept H^+, which means they must have a lone pair of electrons.
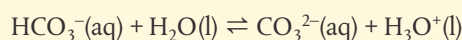
So substances that are amphiprotic according to Brønsted–Lowry theory must possess both a lone pair of electrons and hydrogen that can be released as H^+.
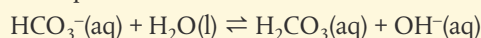
Worked example

Write equations to show HCO_3^- acting (a) as a Brønsted–Lowry acid and (b) as a Brønsted–Lowry base.

Solution

(a) to act as an acid, it donates H^+

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(l)$$

(b) to act as a base, it accepts H^+

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

Exercises

1   Deduce the formula of the conjugate acid of the following:

   (a) SO_3^{2-} **(c)** $C_2H_5COO^-$ **(e)** F^-
   (b) CH_3NH_2 **(d)** NO_3^- **(f)** HSO_4^-

2   Deduce the formula of the conjugate base of the following:

   (a) H_3PO_4 **(c)** H_2SO_3 **(e)** OH^-
   (b) CH_3COOH **(d)** HSO_4^- **(f)** HBr

3   For each of the following reactions, identify the Brønsted–Lowry acids and bases and the conjugate acid–base pairs:

   (a) $CH_3COOH + NH_3 \rightleftharpoons NH_4^+ + CH_3COO^-$
   (b) $CO_3^{2-} + H_3O^+ \rightleftharpoons H_2O + HCO_3^-$
   (c) $NH_4^+ + NO_2^- \rightleftharpoons HNO_2 + NH_3$

4   Show by means of equations how the anion in K_2HPO_4 is amphiprotic.

8.2   Properties of acids and bases

Understandings:

● Most acids have observable characteristic chemical reactions with reactive metals, metal oxides, metal hydroxides, hydrogen carbonates, and carbonates.

   Guidance
   Bases which are not hydroxides, such as ammonia, soluble carbonates, and hydrogen carbonates should be covered.

● Salt and water are produced in exothermic neutralization reactions.

Applications and skills:

● Balancing chemical equations for the reaction of acids.
● Identification of the acid and base needed to make different salts.
● Candidates should have experience of acid–base titrations with different indicators.
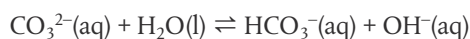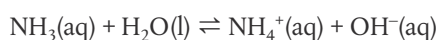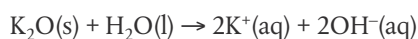
   Guidance
   The colour changes of different indicators are given in the data booklet in section 22.

While we have commented that ideas regarding the defining nature of acids and bases have been long debated, the recognition of what these substances *do* has been known for centuries.

We will look here at some typical reactions of acids and bases in aqueous solutions where H^+ is the ion common to all acids. The bases considered here are those that neutralize acids to produce water, which include:

- metal oxides and hydroxides;
- ammonia;
- soluble carbonates (Na_2CO_3 and K_2CO_3) and hydrogencarbonates ($NaHCO_3$ and $KHCO_3$).

The soluble bases are known as **alkalis**. When dissolved in water they all release the hydroxide ion OH^-. For example:

$$K_2O(s) + H_2O(l) \rightarrow 2K^+(aq) + 2OH^-(aq)$$

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

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

$$HCO_3^-(aq) \rightleftharpoons CO_2(g) + OH^-(aq)$$
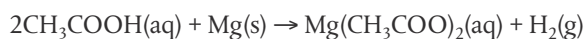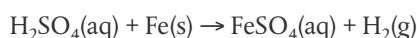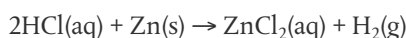
Acids react with metals, bases, and carbonates to form salts

The term **salt** refers to the ionic compound formed when the hydrogen of an acid is replaced by a metal or another positive ion. Salts form by reaction of acids with metals or bases. The familiar example, sodium chloride, NaCl, known as common salt, is derived from the acid HCl by reaction with a base that contains Na, such as NaOH. The terms **parent acid** and **parent base** are sometimes used to describe this relationship between an acid, a base, and their salt.

parent base   parent acid
NaOH   HCl
H_2O
NaCl
salt
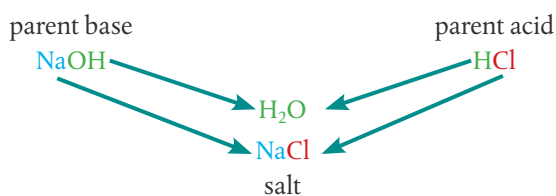
There are three main types of reaction by which acids react to form salts.

1   Acid + metal → salt + hydrogen

$$2HCl(aq) + Zn(s) \rightarrow ZnCl_2(aq) + H_2(g)$$

$$H_2SO_4(aq) + Fe(s) \rightarrow FeSO_4(aq) + H_2(g)$$

$$2CH_3COOH(aq) + Mg(s) \rightarrow Mg(CH_3COO)_2(aq) + H_2(g)$$

We can also write these as ionic equations. For example:
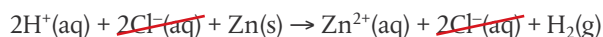
$$2H^+(aq) + 2Cl^-(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + 2Cl^-(aq) + H_2(g)$$

Figure 8.2 The relationship between alkalis and bases.

Alkalis are bases that dissolve in water to form the hydroxide ion OH^-.

In acid–base theory the words ionization and dissociation are often used interchangeably as acid dissociation always leads to ion formation.

Magnesium reacting with HCl.

$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$
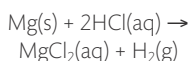
The tiny bubbles are hydrogen gas being liberated.

Acid + reactive metal → salt + hydrogen

Bee stings are slightly acidic, and so have traditionally been treated by using a mild alkali such as baking soda ($NaHCO_3$). Wasp stings, on the other hand, are claimed to be alkali, and so are often treated with the weak acid, ethanoic acid (CH_3COOH) found in vinegar. Whether these claims are valid is, however, open to dispute as the pH of wasp stings is actually very close to neutral. Nonetheless the healing powers of vinegar are well documented and vigorously defended.
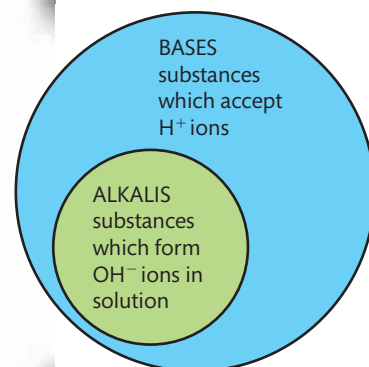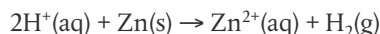
Acid + carbonate → salt + water + carbon dioxide

Neutralization reactions occur when an acid and base react together to form a salt and water. They are exothermic reactions.
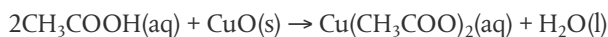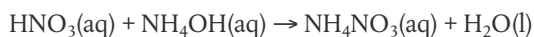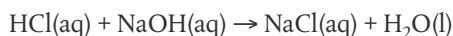
Species which do not change during a reaction, like Cl⁻ here, are called **spectator ions** and can be cancelled out. So the net reaction is:

$$2H^+(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + H_2(g)$$

These reactions of metals with acids are the reason why acids have corrosive properties on most metals, and why, for example, it is important to keep car battery acid well away from the metal bodywork of the car.

You can demonstrate the release of hydrogen from acids in simple experiments by adding a small piece of metal to a dilute solution of the acid. There is a big range, however, in the reactivity of metals in these reactions. More reactive metals such as sodium and potassium in Group 1 would react much too violently, while copper and other less reactive metals such as silver and gold will usually not react at all. This is partly why these less reactive metals are so valuable – they are much more resistant to corrosion. We will consider this differing reactivity in Chapter 9. Another point to note is that although the common acid nitric acid, HNO_3, does react with metals, it usually does not release hydrogen owing to its oxidizing properties (Chapter 9).

2   Acid + base → salt + water

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

$$HNO_3(aq) + NH_4OH(aq) \rightarrow NH_4NO_3(aq) + H_2O(l)$$

$$2CH_3COOH(aq) + CuO(s) \rightarrow Cu(CH_3COO)_2(aq) + H_2O(l)$$

These reactions between acids and bases are known as **neutralization** reactions. They can all be represented by one common ionic equation that shows the net reaction clearly:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$
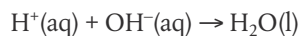
Neutralization reactions of acids with bases are exothermic – heat is released. The **enthalpy of neutralization** is defined as the enthalpy change that occurs when an acid and a base react together to form one mole of water. For reactions between all strong acids and strong bases, the enthalpy change is very similar with $\Delta H = -57$ kJ mol⁻¹ approximately. This is because the net reaction is the same, involving the formation of water from its ions.

There are times when neutralization reactions are useful to help reduce the effect of an acid or a base. For example, treatment for acid indigestion often involves using 'antacids' which contain a mixture of weak alkalis such as magnesium hydroxide and aluminium hydroxide. As we will learn in section 8.5, in places where the soil has become too acidic, the growth of many plants will be restricted. Adding a weak alkali such as lime, CaO, can help to reduce the acidity and so increase the fertility of the soil.

3   Acid + carbonate → salt + water + carbon dioxide

$$2HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

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

$$CH_3COOH(aq) + KHCO_3(aq) \rightarrow KCH_3COO(aq) + H_2O(l) + CO_2(g)$$
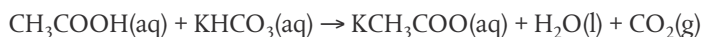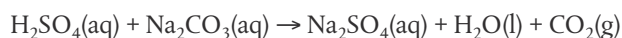
These reactions can also be represented as an ionic equation:

$$2H^+(aq) + CO_3^{2-}(aq) \rightarrow H_2O(l) + CO_2(g)$$
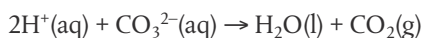
The reactions, like the reaction of acids with metals, involve a gas being given off so they visibly produce bubbles, known as **effervescence**.

Rain water dissolves some carbon dioxide from the air to form a weak solution of carbonic acid, H_2CO_3.

$$H_2O(l) + CO_2(g) \rightleftharpoons H_2CO_3(aq)$$
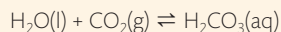
Greater pressure, such as that found in capillary beds of limestone ($CaCO_3$) rocks, increases the tendency of CO_2 to dissolve, giving rise to a more acidified solution. This then reacts on the limestone as follows:

$$H_2CO_3(aq) + CaCO_3(s) \rightleftharpoons Ca(HCO_3)_2(aq)$$

$CaCO_3$, limestone, is virtually insoluble whereas the product calcium hydrogencarbonate, $Ca(HCO_3)_2$, is soluble and washes away, leading to erosion of the rocks. This is why caves commonly form in limestone regions. Inside the cave where the pressure is lower, the reaction above may be reversed, as less CO_2 dissolves. In this case $CaCO_3$ comes out of solution and precipitates, giving rise to the formations known as stalagtites and stalagmites.
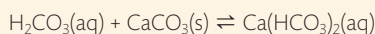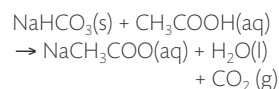
Similar reactions of rain water dissolving $CaCO_3$ rocks can give rise to water supplies with elevated levels of Ca^{2+} ions, known as 'hard water'.

In section 8.5, these reactions between acids and metals and metal carbonates are discussed in the context of the environmental problem known as acid deposition.

Acids and bases can be distinguished using indicators

Indicators act as chemical detectors, giving information about a change in the environment. The indicators most widely used in chemistry are **acid–base indicators** that change colour reversibly according to the concentration of H^+ ions in the solution. This happens because they are weak acids and bases whose conjugates have different colours. The colour change means that they can be used to identify the pH of a substance. Indicators are generally used either as aqueous solutions or absorbed onto 'test paper'.

Probably the best known acid–base indicator is **litmus**, which is a dye derived from lichens, and which turns pink in the presence of acid and blue in the presence of alkalis. It is widely used to test for acids or alkalis, but is not so useful in distinguishing between different strengths of acid or alkali.

Other indicators give different colours in different solutions of acid and alkali. Some common examples are given in the table here, and there are more in section 22 of your IB data booklet.

Indicator	Colour in acid	Colour in alkali
litmus	pink	blue
methyl orange	red	yellow
phenolphthalein	colourless	pink

Many of these indicators are derived from natural substances such as extracts from flower petals and berries. A common indicator in the laboratory is **universal indicator**, which is formed by mixing together several indicators. It changes colour

▲ Kitchen chemistry. Baking soda ($NaHCO_3$) and vinegar (CH_3COOH) react together in a powerful acid–base reaction, releasing carbon dioxide gas.

$NaHCO_3(s) + CH_3COOH(aq)$
$\rightarrow NaCH_3COO(aq) + H_2O(l)$
$+ CO_2 (g)$

▲ Limestone rock shaped by natural chemical erosion in Switzerland. Rainwater, a weak solution of H_2CO_3, reacts with the calcium carbonate, slowly dissolving it.

many times across a range of different acids and alkalis and so can be used to measure the concentration of H^+ on the pH scale. We will discuss this later in the chapter.

In section 18.3 (page 378), we will learn in more detail how indicators work and how they are used in quantitative experimental work.

Litmus indicator compared in acidic and alkaline solutions.

> Be careful not to assume that indicator tests always show acids as pink and alkalis as blue. This is true with litmus, but other indicators give many different colours including pink in alkali.

Acid–base titrations are based on neutralization reactions

Neutralization reactions are often used in the laboratory to calculate the exact concentration of an acid or an alkali when the other concentration is known. As we learned in Chapter 1, the solution of known concentration is known as the standard solution. The technique known as **acid–base titration** involves reacting together a carefully measured volume of one of the solutions, and adding the other solution gradually until the so-called **equivalence point** is reached where they exactly neutralize each other. A convenient way to determine when the equivalence point has been reached is to use an indicator, chosen to change colour as the acid and base exactly neutralize each other.

Figure 8.3 Simple titration apparatus.
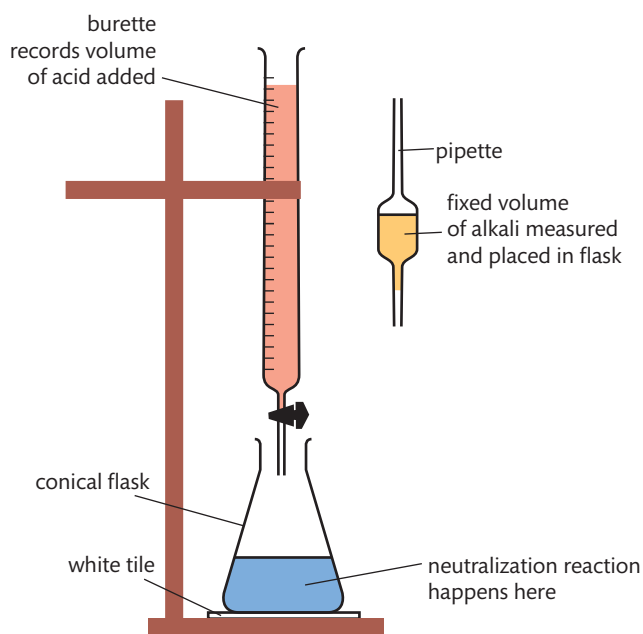
For example, titration can be used in the following experiments:

- to calculate the concentration of ethanoic acid in vinegar by titration with a standard solution of aqueous sodium hydroxide, using phenolphthalein indicator;
- to calculate the concentration of sodium hydroxide by titration with a standard solution of hydrochloric acid, using methyl orange indicator.

A good indicator is one that gives a distinct or sharp colour change at the equivalence point.

In section 18.3 we will study additional examples of titrations and learn how to choose an indicator that is appropriate for specific combinations of acid and base.

> **Acid–base titration to calculate the concentration of ethanoic acid in vinegar**
>
> Full details of how to carry out this experiment with a worksheet are available online.

5 Write equations for the following reactions:

(a) sulfuric acid and copper oxide
(b) nitric acid and sodium hydrogencarbonate
(c) phosphoric acid and potassium hydroxide
(d) ethanoic acid and aluminium

6 An aqueous solution of which of the following reacts with calcium metal?

A ammonia
B hydrogen chloride
C potassium hydroxide
D sodium hydrogencarbonate

7 Which of the following is / are formed when a metal oxide reacts with a dilute acid?

I   a metal salt
II   water
III carbon dioxide gas

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

8 Suggest by name a parent acid and parent base that could be used to make the following salts. Write equations for each reaction.

(a) sodium nitrate
(b) ammonium chloride
(c) copper(II) sulfate
(d) potassium methanoate

> **!** When you need to choose a base in solution to make a specific salt, it is useful to know some simple solubility rules.
>
> • The only soluble carbonates and hydrogencarbonates are $(NH_4)_2CO_3$, Na_2CO_3, K_2CO_3, $NaHCO_3$, $KHCO_3$, and $Ca(HCO_3)_2$.
>
> • The only soluble hydroxides are NH_4OH, $LiOH$, $NaOH$, and KOH.

8.3 The pH scale

Understandings:

• pH = $-\log [H^+(aq)]$ and $[H^+] = 10^{-pH}$.
• A change of one pH unit represents a 10-fold change in the hydrogen ion concentration $[H^+]$.

Guidance
Knowing the temperature dependence of K_w is not required.

• pH values distinguish between acidic, neutral, and alkaline solutions.
• The ionic product constant, $K_w = [H^+][OH^-] = 10^{-14}$ at 298 K.

Applications and skills:

• Solving problems involving pH, $[H^+]$, and $[OH^-]$.

Guidance
• *Students should be concerned only with strong acids and bases in this sub-topic.*
• *Students will not be assessed on pOH values.*

• Students should be familiar with the use of a pH meter and universal indicator.

pH is a logarithmic expression of [H⁺]

Chemists realized a long time ago that it would be useful to have a quantitative scale of acid strength based on the concentration of hydrogen ions. As the majority of acids encountered are weak, the hydrogen ion concentration expressed directly as mol dm^{-3} produces numbers with large negative exponents; for example the H^+ concentration in our blood is 4.6×10^{-8} mol dm^{-3}. Such numbers are not very user-friendly when it comes to describing and comparing acids. The introduction of the pH scale in 1909 by Sorensen led to wide acceptance owing to its ease of use. It is defined as follows:

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

> **ⓘ** The Danish chemist Søren Peder Lauritz Sorensen (1868–1939) developed the pH concept in 1909, originally proposing that it be formulated as p_H. He did not account for his choice of the letter 'p' though it has been suggested to originate from the German word *potenz* for power. It could equally well derive from the Latin, Danish, or French terms for the same word.

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

$[H^+]$

pH

Figure 8.4 The inverse relationship between pH and H^+.

Figure 8.5 The pH scale at 298 K and pH values of some common substances.

$[H^+]$ pH

$[H^+]$	pH	
10^{-14}	14	1.0 mol dm^{-3} KOH
10^{-13}	13	
10^{-12}	12	oven cleaner
		household ammonia
10^{-11}	11	
10^{-10}	10	milk of magnesia
10^{-9}	9	
10^{-8}	8	baking soda (NaHCO$_3$)
		toothpaste
10^{-7}	7	human blood
		pure water, NaCl$_{(aq)}$
10^{-6}	6	
10^{-5}	5	rainwater
10^{-4}	4	tomatoes
		wine, beer
10^{-3}	3	vinegar
10^{-2}	2	lemon juice
		stomach acid
10^{-1}	1	car battery acid
$10^0 = 1$	0	1.0 mol dm^{-3} HCl

basic / neutral / acidic

In other words, pH is the negative number to which the base 10 is raised to give the $[H^+]$. This can also be expressed as:

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

- A solution that has $[H^+] = 0.1$ mol dm$^{-3} \Rightarrow [H^+] = 10^{-1}$ mol dm$^{-3} \Rightarrow$ pH = 1.
- A solution that has $[H^+] = 0.01$ mol dm$^{-3} \Rightarrow [H^+] = 10^{-2}$ mol dm$^{-3} \Rightarrow$ pH = 2.

Now we can explore some of the features of the pH scale that help to make it so convenient.

pH numbers are usually positive and have no units

Although the pH scale is theoretically an infinite scale (and can even extend into negative numbers), most acids and bases encountered will have positive pH values and fall within the range 0–14, corresponding to $[H^+]$ from 1.0 mol dm^{-3} to 10^{-14} mol dm^{-3}.

The pH number is inversely related to the $[H^+]$

Solutions with a higher $[H^+]$ have a lower pH and vice versa. So stronger and more concentrated acids have a lower pH, weaker and more dilute acids have a higher pH.

A change of one pH unit represents a 10-fold change in $[H^+]$

This means increasing the pH by one unit represents a decrease in $[H^+]$ by 10 times; decreasing by one pH unit represents an increase in $[H^+]$ by 10 times.
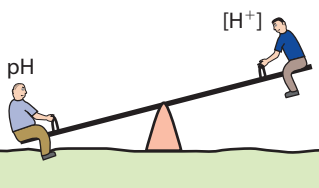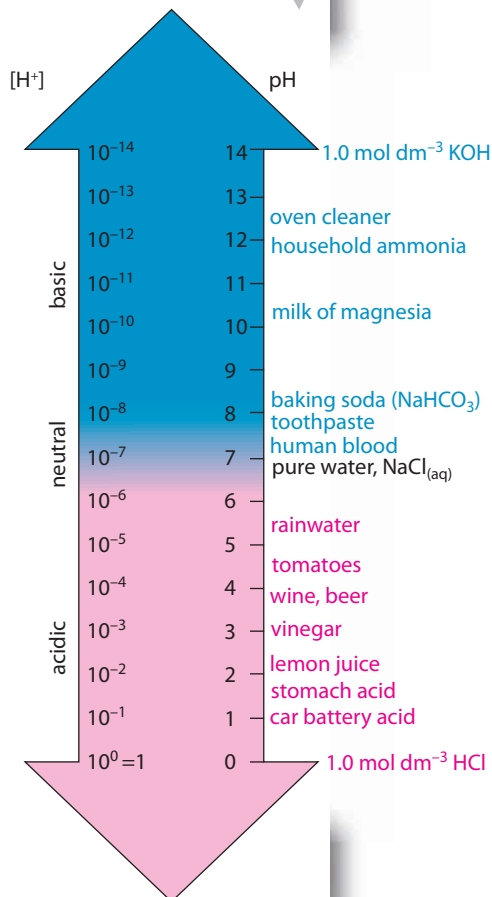
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The use of a logarithmic scale to represent data enables a wide range of values to be presented as a smaller range of simpler numbers. We see here that the pH scale takes a range of hydrogen ion concentrations from 10^0 to 10^{-14} and effectively compresses it to a much smaller scale of numbers, 0–14. On page 88, we saw that the use of a logarithmic scale to represent the ionization energies of aluminium similarly makes a wide range of data easier to interpret. In cases of exponential change, a log base scale shows the data as a straight line, so outliers where the change is greater or less than exponential can be easily identified.

But use of a logarithmic scale can also be misleading, as it can obscure the scale of change if not interpreted correctly. For example, a small change in pH represents a dramatic difference in the hydrogen ion concentration of a solution. Keep this in mind when you read reports of changes in pH, for example of rainfall as a result of pollution. A reported change from pH 5.5 to pH 4.5 may not sound much, but in fact it represents a *ten-fold increase* in the hydrogen ion concentration – hugely significant to the acidic properties. As we will learn in section 18.3 (page 378), the pH of our blood is carefully controlled by chemicals called buffers to remain at 7.4; a change of only half a pH unit on either side of this is known to be fatal. Communication of data in science takes different forms and uses different scales, and must always be interpreted in the context used.

Logarithmic scales are used in other disciplines where they can help in the presentation of data. In medicine, the logarithmic decay of levels of drugs in the blood against time is used. In seismic studies, the Richter scale is a logarithmic expression of the relative energy released during earthquakes. In sense perception the decibel scale of sound intensity and the scale for measuring the visible brightness of stars (their magnitude) are also logarithmic scales.

Worked example

If the pH of a solution is changed from 3 to 5, deduce how the hydrogen ion concentration changes.

Solution

pH = 3 $\Rightarrow$ [H^+] = 10^{-3} mol dm^{-3}; pH = 5 $\Rightarrow$ [H^+] = 10^{-5} mol dm^{-3}

So [H^+] has changed by 10^{-2} or decreased by 100.

The pH scale is a measure of [H^+] and so at first glance may appear to be more suited for the measurement of acids than of bases. But we can in fact use the same scale to describe the alkalinity of a solution. As will be explained on page 359, this is because the relationship between [H^+] and [OH^-] is inverse in aqueous solutions, and so lower [H^+] (higher pH) means higher [OH^-] and vice versa. Therefore the scale of pH numbers represents a range of values from strongly acidic through to strongly alkaline.

pH 0	**pH 7**	**pH 14**
increasing [H^+] **increasing acidity**	**neutral**	**increasing [OH^-]** **increasing alkalinity**

pH calculations

From the definition of pH we can:

(i) calculate the value of pH from a known concentration of H^+;

(ii) calculate the concentration of H^+ from a given pH.

Worked example

A sample of lake water was analysed at 298 K and found to have [H^+] = 3.2×10^{-5} mol dm^{-3}. Calculate the pH of this water and comment on its value.

Solution

$$pH = -\log_{10} [H^+]$$
$$= -\log_{10} (3.2 \times 10^{-5}) = -(-4.49485)$$
$$pH = 4.49$$

At 298 K this pH < 7, and the lake water is therefore acidic.

Worked example

Human blood has a pH of 7.40. Calculate the concentration of hydrogen ions present.

Solution

$$[H^+] = 10^{-pH}$$
$$= 10^{-7.40} = 4.0 \times 10^{-8}$$
$$[H^+] = 4.0 \times 10^{-8} \text{ mol dm}^{-3}$$

In the last 40 years, researchers have developed so-called 'super acids' by mixing together various substances. These are several orders of magnitude more acidic than conventional acids, and one example known as 'magic acid' is even able to dissolve candle wax.

In pH calculations you will need to be able to work out logarithms to base 10 and anti-logarithms. Make sure that you are familiar with these operations on your calculator.

Note that the logarithms used in all the work on acids and bases are logarithms to base 10 (log). Do not confuse these with natural logarithms, to base e, (ln).

The rule to follow for significant figures in logarithms is that *the number of decimal places in the logarithm should equal the number of significant figures in the number*. In other words, the number to the left of the decimal place in the logarithm is not counted as a significant figure (this is because it is derived from the exponential part of the number). In the first example here, the number given has two significant figures (3.2) and so the answer is given to two decimal places (.49).

Measuring pH

An easy way to measure pH is with universal indicator paper or solution. The substance tested will give a characteristic colour, which can then be compared with a colour chart supplied with the indicator. Narrower range indicators give a more accurate reading than broad range, but they always depend on the ability of the user's eyes to interpret the colour.

A more objective and usually more accurate means is by using a **pH meter** or probe that directly reads the [H⁺] concentration through a special electrode. pH meters can record to an accuracy of several decimal points. They must, however, be calibrated before each use with a buffer solution, and standardized for the temperature, as pH is a temperature-dependent measurement.

A digital probe showing a pH of 3.20 for the solution in the beaker. The temperature dial is adjusted to the room temperature, allowing the pH meter to compensate for the temperature.

The pH scale and universal indicator. The tubes contain universal indicator added to solutions of pH 0–14 from left to right

The ionization of water

Victoria Falls on the Zimbabwe–Zambia border. It is estimated that 6.25×10^8 dm³ of water flow over the falls every minute. According to the ionization constant discussed here, for every billion of these molecules only two are ionized, and that proportion gets even smaller at lower temperatures.

As the majority of acid–base reactions involve ionization in aqueous solution, it is useful to consider the role of water in more detail. Water itself does ionize, albeit only very slightly at normal temperatures and pressures, so we can write an equilibrium expression for this reaction.

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

We are using $H^+(aq)$ throughout this chapter as a simplified form of $H_3O^+(aq)$. This is acceptable in most situations, but don't forget that H^+ in aqueous solution always exists as $H_3O^+(aq)$.
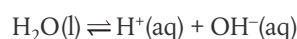
Therefore $K_c = \dfrac{[H^+][OH^-]}{[H_2O]}$

The concentration of water can be considered to be constant due to the fact that so little of it ionizes, and it can therefore be combined with K_c to produce a modified equilibrium constant known as K_w.

$$K_c[H_2O] = [H^+][OH^-]$$
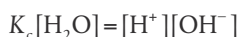
Therefore $K_w = [H^+][OH^-]$

K_w is known as the **ionic product constant of water** and has a fixed value at a specified temperature. At 298 K, $K_w = 1.00 \times 10^{-14}$.

In pure water because $[H^+] = [OH^-]$, it follows that $[H^+] = \sqrt{K_w}$

So, at 298 K, $[H^+] = 1.00 \times 10^{-7}$ which gives pH = 7.00

This is consistent with the widely known value for the pH of water at room temperature.

The relationship between H⁺ and OH⁻ is inverse

Because the product $[H^+] \times [OH^-]$ gives a constant value, it follows that the concentrations of these ions must have an inverse relationship. In other words, in aqueous solutions the higher the concentration of H^+ the lower the concentration of OH^-. Solutions are defined as acidic, neutral, or basic according to their relative concentrations of these ions as shown below.

		at 298 K
Acidic solutions are defined as those in which	$[H^+] > [OH^-]$	pH < 7
Neutral solutions are defined as those in which	$[H^+] = [OH^-]$	pH = 7
Alkaline solutions are defined as those in which	$[H^+] < [OH^-]$	pH > 7

So if we know the concentration of either H^+ or OH^-, we can calculate the other from the value of K_w.

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

Worked example

A sample of blood at 298 K has $[H^+] = 4.60 \times 10^{-8}$ mol dm^{-3}.

Calculate the concentration of OH^- and state whether the blood is acidic, neutral, or basic.

Solution

At 298 K, $K_w = 1.00 \times 10^{-14} = [H^+][OH^-]$

$$[OH]^- = \frac{1.00 \times 10^{-14}}{4.60 \times 10^{-8}} = 2.17 \times 10^{-7} \text{ mol dm}^{-3}$$

As $[OH^-] > [H^+]$ the solution is basic.

Calculations involving $[H^+]$, $[OH^-]$, and pH, as well as the pOH scale, are considered in more detail in section 18.2, page 366.

Water is a pure liquid so its concentration is just a function of its density, which is 1.00 g cm^{-3}.

From $n = \frac{m}{M}$, this gives

$n(H_2O) = \frac{1000}{18}$ in 1 dm^3

so concentration (H_2O) = 55 mol dm^{-3}.

The value $K_w = 1.00 \times 10^{-14}$ at 298 K is given in section 2 of the IB data booklet so does not have to be learned.

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

The concentrations of H⁺ and OH⁻ are inversely proportional in an aqueous solution.

Exercises

9 What happens to the pH of an acid when 10 cm³ of it is added to 90 cm³ of water?

10 Beer has a hydrogen ion concentration of 1.9×10^{-5} mol dm⁻³. What is its pH?

11 An aqueous solution has a pH of 9 at 25 °C. What are its concentrations for H⁺ and OH⁻?

12 For each of the following aqueous solutions, calculate [OH⁻] from [H⁺] or [H⁺] from [OH⁻]. Classify each solution as acidic, basic, or neutral at 298 K.

    (a) $[H^+] = 3.4 \times 10^{-9}$ mol dm⁻³

    (b) $[OH^-] = 0.010$ mol dm⁻³

    (c) $[OH^-] = 1.0 \times 10^{-10}$ mol dm⁻³

    (d) $[H^+] = 8.6 \times 10^{-5}$ mol dm⁻³

13 What is the pH of 0.01 mol dm⁻³ solution of HCl which dissociates fully?

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

14 For each of the following biological fluids, calculate the pH from the given concentration of H⁺ or OH⁻ ions.

    (a) bile: $[OH^-] = 8 \times 10^{-8}$ mol dm⁻³

    (b) gastric juice: $[H^+] = 10^{-2}$ mol dm⁻³

    (c) urine: $[OH^-] = 6 \times 10^{-10}$ mol dm⁻³

15 A solution of sodium hydroxide is prepared by adding distilled water to 6.0 g NaOH to make 1.0 dm³ of solution. What is the pH of this solution? Assume that NaOH dissociates completely in solution:

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

8.4 Strong and weak acids and bases

Understandings:

- Strong and weak acids and bases differ in the extent of ionization.

  Guidance

  The terms ionization and dissociation can be used interchangeably.

- Strong acids and bases of equal concentrations have higher conductivities than weak acids and bases.

  Guidance

  See section 21 in the data booklet for a list of weak acids and bases.

- A strong acid is a good proton donor and has a weak conjugate base.
- A strong base is a good proton acceptor and has a weak conjugate acid.

Applications and skills:

- Distinction between strong and weak acids and bases in terms of the rates of their reactions with metals, metal oxides, metal hydroxides, metal hydrogen carbonates, and metal carbonates and their electrical conductivities for solutions of equal concentrations.

The strength of an acid or base depends on its extent of ionization

We have seen that the reactions of acids and bases are dependent on the fact that they dissociate in solution, acids to produce H⁺ ions and bases to produce OH⁻ ions. As we will see here, the extent of this dissociation is what defines the strength of an acid or a base.

Consider the acid dissociation reaction:

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$$
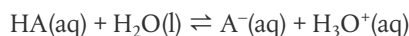
If this acid dissociates fully, it will exist entirely as ions in solution. It is said to be a **strong acid**. For example, hydrochloric acid, HCl, is a strong acid.

The reaction is written without the equilibrium sign.

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$
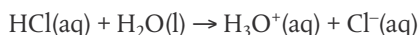
If, on the other hand, the acid dissociates only partially, it produces an equilibrium mixture in which the undissociated form dominates. It is said to be a **weak acid**. For example, ethanoic acid, CH_3COOH, is a weak acid.
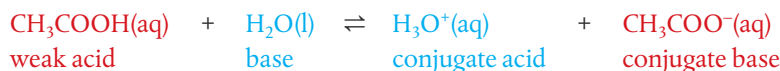
$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$
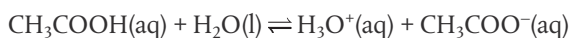
Here it is essential to use the equilibrium sign for its dissociation reaction.

Strong acids are good proton donors. As their dissociation reactions go to completion, their conjugate bases are not readily able to accept a proton. For example, HCl reacts to form the conjugate base Cl^-, which shows virtually no basic properties.

$$HCl(aq) \quad + \quad H_2O(l) \quad \rightarrow \quad H_3O^+(aq) \quad + \quad Cl^-(aq)$$
strong acid base conjugate acid conjugate base

Weak acids are poor proton donors. As their dissociation reactions are equilibria which lie to the left, in favour of reactants, their conjugate bases are readily able to accept a proton. For example, CH_3COOH reacts to form the conjugate base CH_3COO^-, which is a stronger base than Cl^-.

$$CH_3COOH(aq) \quad + \quad H_2O(l) \quad \rightleftharpoons \quad H_3O^+(aq) \quad + \quad CH_3COO^-(aq)$$
weak acid base conjugate acid conjugate base

So acid dissociation reactions favour the production of the weaker conjugate.

In a similar way, bases can be described as strong or weak on the basis of the extent of their ionization. For example, NaOH is a **strong base** because it ionizes fully.

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

Its dissociation is written without equilibrium signs.

(Note that it is the OH^- ions that show Brønsted–Lowry base behaviour by accepting protons.)

On the other hand, NH_3 is a **weak base** as it ionizes only partially, so its equilibrium lies to the left and the concentration of ions is low.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
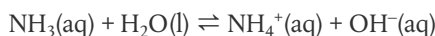
Strong bases are good proton acceptors; they react to form conjugates that do not show acidic properties. Weak bases are poor proton acceptors; they react to form conjugates with stronger acidic properties than the conjugates of strong bases. Base ionization reactions favour the production of the weaker conjugate.

In section 18.2 (page 366), we will learn how we can quantify the strength of an acid or base in terms of the equilibrium constant for its dissociation reaction, and look in more detail at the relationship between the strength of acid–base conjugate pairs.

The strength of an acid or base is therefore a measure of how readily it dissociates in aqueous solution. This is an inherent property of a particular acid or base, dependent on its bonding. Do not confuse acid or basic *strength* with its *concentration*, which is a variable depending on the number of moles per unit volume, according to how much solute has been added to the water. Note, for example, it is possible for an acid or base

Strong acids and strong bases ionize almost completely in solution; weak acids and weak bases ionize only partially in solution.

In writing the ionization reactions of weak acids and bases, it is essential to use the equilibrium sign.

to be strong but present in a dilute solution, or weak and present in a concentrated solution.

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The use of advanced analytical techniques has allowed the strengths of different acids and bases to be quantified and compared. Experimental evidence has been obtained from accurate pH and concentration measurements. Sometimes the results may seem surprising, and this has led to a fuller exploration of the factors involved at the molecular level. For example, the relative acidic strengths of the hydrogen halides (HF, HCl, HBr, and HI) are found to increase down the group, despite the decreasing polarity of the molecules. This is explained by the decreasing bond strength of H–halogen as the halogen atom increases in size. In other cases, such as the organic acids, factors such as electronegativity, ion stability, and inductive effects are used to explain the patterns in acid strength. Theories must explain experimental evidence and be subject to testable predictions.

Weak acids and bases are much more common than strong acids and bases

It is often useful to know which of the acids and bases we come across are strong and which are weak. Fortunately this is quite easy as there are very few common examples of strong acids and bases, so this short list can be committed to memory. You will then know that any other acids and bases you come across are likely to be weak.

	Acid		Base	
common examples of **strong** forms	HCl	hydrochloric acid	LiOH	lithium hydroxide
	HNO_3	nitric acid	NaOH	sodium hydroxide
	H_2SO_4	sulfuric acid	KOH	potassium hydroxide
			$Ba(OH)_2$	barium hydroxide
some examples of **weak** forms	CH_3COOH and other organic acids	ethanoic acid	NH_3	ammonia
	H_2CO_3	carbonic acid	$C_2H_5NH_2$ and other amines	ethylamine
	H_3PO_4	phosphoric acid		

Note that amines such as ethylamine, $C_2H_5NH_2$, can be considered as organic derivatives of NH_3 in which one of the hydrogen atoms has been replaced by an alkyl (hydrocarbon) group. There are literally hundreds of acids and bases in organic chemistry (Chapter 10), nearly all of which are weak in comparison with the strong inorganic acids listed here. Many of these are listed in section 21 of the IB data booklet. Amino acids, the building blocks of proteins, as their name implies contain both the basic –NH_2 amino group and the –COOH acid group. The 'A' in DNA, the store of genetic material, stands for 'acid', in this case the acid present is phosphoric acid.

Distinguishing between strong and weak acids and bases

Due to their greater ionization in solution, strong acids and strong bases will contain a *higher concentration of ions* than weak acids and weak bases. This then can be used as

a means of distinguishing between them. Note though that such comparisons will only be valid when solutions of the same concentration (mol dm^{-3}) are compared at the same temperature. We will consider here three properties that depend on the concentration of ions and so can be used for this purpose.

1 Electrical conductivity

Electrical conductivity of a solution depends on the concentration of mobile ions. Strong acids and strong bases will therefore show higher conductivity than weak acids and bases – so long as solutions of the same concentration are compared. This can be measured using a conductivity meter or probe, or by using the conductivity setting on a pH meter.

2 Rate of reaction

The reactions of acids described in section 8.2 depend on the concentration of H$^+$ ions. They will therefore happen at a greater rate with stronger acids.

These different rates of reactions may be an important consideration, for example, regarding safety in the laboratory, but they usually do not provide an easy means of quantifying data to distinguish between weak and strong acids.

3 pH

Because it is a measure of the H$^+$ concentration, the pH scale can be used directly to compare the strengths of acids (providing they are of equal molar concentration). Remember the higher the H$^+$ concentration, the lower the pH value. Universal indicator or a pH meter can be used to measure pH.

▲ The different rates of reaction between magnesium metal and hydrochloric acid and ethanoic acid. The mass and surface area of the magnesium added and the concentrations and volumes of the acids are equal in both tubes. The higher rate with the strong acid HCl is shown on the left, where large bubbles of hydrogen form. The slower reaction with CH$_3$COOH, shown on the right, causes smaller bubbles of hydrogen gas, which gives the milky appearance.

Exercises

16 Which of the following 1 mol dm^{-3} solutions will be the poorest conductor of electricity?

A HCl   **B** CH$_3$COOH   **C** NaOH   **D** NaCl

17 Which methods will distinguish between equimolar solutions of a strong base and a strong acid?

   I   Add magnesium to each solution and look for the formation of gas bubbles.
   II   Add aqueous sodium hydroxide to each solution and measure the temperature change.
   III   Use each solution in a circuit with a battery and lamp and see how brightly the lamp glows.

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

18 Which acid in each of the following pairs has the stronger conjugate base?

   (a) H$_2$CO$_3$ or H$_2$SO$_4$
   (b) HCl or HCOOH

18.1 Lewis acids and bases

Understandings:
- A Lewis acid is a lone pair acceptor and a Lewis base is a lone pair donor.

  Guidance
  - *Relations between Brønsted–Lowry and Lewis acids and bases should be discussed.*
  - *Both organic and inorganic examples should be studied.*
- When a Lewis base reacts with a Lewis acid a coordinate bond is formed.
- A nucleophile is a Lewis base and an electrophile is a Lewis acid.

Applications and skills:

- Application of Lewis acid–base theory to inorganic and organic chemistry to identify the role of the reacting species.

Lewis theory focuses on electron pairs

Gilbert Lewis, whose name famously belongs to electron dot structures for representing covalent bonding (Chapter 4), used such structures in interpreting Brønsted–Lowry theory. Realizing that the base must have a lone pair of electrons, he reasoned that the entire reaction could be viewed in terms of the electron pair rather than in terms of proton transfer. For example, the reaction previously described in which ammonia acts as a base can be represented as follows:
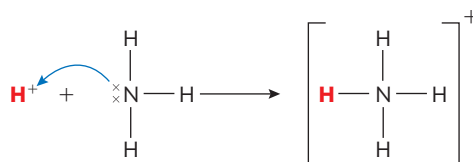
The curly arrow (shown in blue) is a convention used to show donation of a pair of electrons. H^+ is acting as an electron pair acceptor and the nitrogen atom in ammonia is acting as an electron pair donor. From such thinking Lewis developed a new, broader definition of acids and bases.

- A Lewis acid is a lone pair acceptor.
- A Lewis base is a lone pair donor.

Lewis bases and Brønsted–Lowry bases are therefore the same group of compounds: by either definition they are species that must have a lone pair of electrons.

In the case of acids, however, the Lewis definition is broader than the Brønsted–Lowry theory: no longer restricted just to H^+, an acid by Lewis definition is any species capable of accepting a lone pair of electrons. Of course this *includes* H^+ with its vacant orbital (so all Brønsted–Lowry acids *are* Lewis acids) – but it will also include molecules that have an incomplete valence shell. Lewis acid–base reactions result in the formation of a covalent bond, which will always be a **coordinate bond** because both the electrons come from the base.

Here is another example:
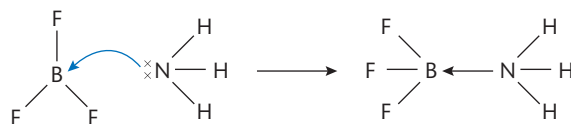
BF_3 has an incomplete octet so is able to act as a Lewis acid and accept a pair of electrons; NH_3 acts as a Lewis base, donating its lone pair of electrons. The arrow on the covalent bond denotes the fact that it is a coordinate bond with both electrons donated from the nitrogen.

Other good examples of Lewis acid–base reactions are found in the chemistry of the transition elements. As we learned in Chapter 3, these metals in the middle of the Periodic Table often form ions with vacant orbitals in their d subshell. So they are able to act as Lewis acids and accept lone pairs of electrons when they bond with ligands to form complex ions.

A Lewis acid is lone pair acceptor. A Lewis base is a lone pair donor.

Make sure that when you are describing Lewis acid–base behaviour you refer to donation and acceptance of an electron *pair*. If you omit the word pair, you would be describing a redox reaction which is entirely different.

Ligands, as donors of lone pairs, are therefore acting as Lewis bases.

For example, Cu^{2+} in aqueous solution reacts as follows:

$$Cu^{2+}(aq) + 6H_2O(l) \rightarrow [Cu(H_2O)_6]^{2+}(aq)$$
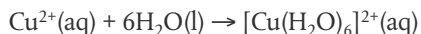
Cu^{2+} is a Lewis acid and H_2O is a Lewis base.

Typical ligands found in complex ions include H_2O, CN^-, and NH_3. Note that these all possess lone pairs of electrons, the defining feature of their Lewis base properties.

Nucleophiles and electrophiles

At about the same time as Lewis developed his acid–base theory, alternate language was being introduced to describe the behaviour of reactants with respect to electron pairs.

A **nucleophile** ('likes nucleus') is an electron-rich species that donates a lone pair to form a new covalent bond in a reaction.

An **electrophile** ('likes electrons') is an electron-deficient species that accepts a lone pair from another reactant to form a new covalent bond.

These terms are often used to describe reactions in terms of electron-rich nucleophiles attacking electron-deficient electrophiles, and are depicted using curly arrows to show electron movements. Several examples from organic chemistry are discussed in Chapter 10.

Clearly these terms are the same as those derived by Lewis. In other words, a nucleophile is a Lewis base and an electrophile is a Lewis acid.

• Examples of nucleophiles / Lewis bases:
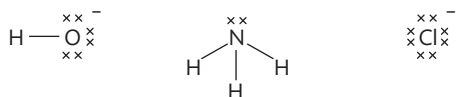
• Examples of electrophiles / Lewis acids:
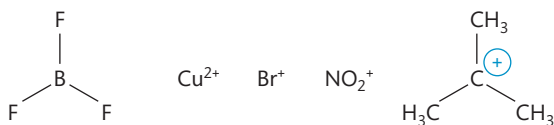
The reaction below shows the hydroxide ion, OH^-, acting as a nucleophile on an organic molecule known as a halogenoalkane. This reaction is discussed in detail on page 498. We can see that OH^- is a Lewis base as it is donating a lone pair of electrons.
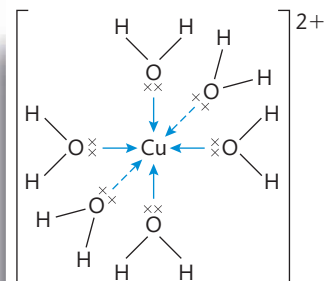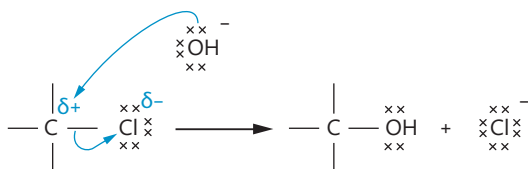
▲ **Figure 8.6** In the complex ion$[Cu(H_2O)_6]^{2+}$, Cu^{2+} has acted as a Lewis acid and the H_2O ligands as Lewis bases. The bonds within the complex ion are coordinate bonds, as indicated by the arrows. For clarity only one lone pair (out of two) is shown on each O atom in H_2O.
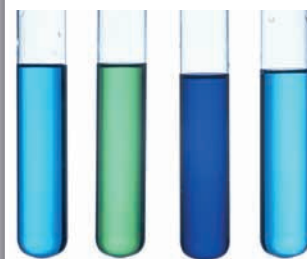
▲ Copper ions (Cu^{2+}) forming different complex ions with distinct colours. From left to right the ligands are H_2O, Cl^-, NH_3, and the organic group EDTA. The Cu^{2+} ion has acted as the Lewis acid, the ligands as Lewis bases.

A nucleophile is a Lewis base and an electrophile is a Lewis acid.

TOK Different approaches and vocabulary can sometimes be used to explain the same phenomenon. Does the use of language as a way of knowing help us to judge these competing approaches?
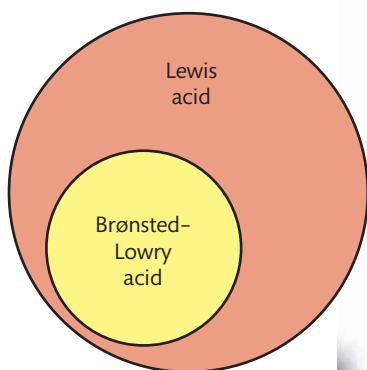
Figure 8.7 Relationship between Brønsted–Lowry acids and Lewis acids.

Comparison of Brønsted–Lowry and Lewis theories of acids and bases

Theory	Definition of acid	Definition of base
Brønsted–Lowry	proton donor	proton acceptor
Lewis	electron pair acceptor	electron pair donor

• Although all Brønsted–Lowry acids are Lewis acids, not all Lewis acids are Brønsted–Lowry acids. The term Lewis acid is usually reserved for those species which can *only* be described by Lewis theory, that is those that do not release H^+.

• Many reactions cannot be described as Brønsted–Lowry acid–base reactions, but do qualify as Lewis acid–base reactions. These are reactions where no transfer of H^+ occurs.

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Lewis acid–base theory is compatible with Brønsted–Lowry theory, it does not falsify it. By changing the perspective of acid–base reactions from the proton to the lone pair of electrons, it opens up a wider field of application. The proton no longer has a central role, it is just one example of a lone pair acceptor. Lewis acids include a wide range of both organic and inorganic species that are not recognized as acids in Brønsted–Lowry theory. Yet, in many cases, as we will see in the following sections, Brønsted–Lowry theory is sufficient and could be considered a more useful theory for the description of acid–base reactions, especially those occurring in aqueous solution.

Exercises

19 For each of the following reactions identify the Lewis acid and the Lewis base.

  (a) $4NH_3(aq) + Zn^{2+}(aq) \rightarrow [Zn(NH_3)_4]^{2+}(aq)$
  (b) $2Cl^-(aq) + BeCl_2(aq) \rightarrow [BeCl_4]^{2-}(aq)$
  (c) $Mg^{2+}(aq) + 6H_2O(l) \rightarrow [Mg(H_2O)_6]^{2+}(aq)$

20 Which of the following could not act as a ligand in a complex ion with a transition metal?

  A Cl^- **B** NCl_3 **C** PCl_3 **D** CH_4

21 Which of the following reactions represents an acid–base reaction according to Lewis theory but not according to Brønsted–Lowry theory?

  A $NH_3(aq) + HCl(aq) \rightleftharpoons NH_4Cl(aq)$
  B $2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$
  C $Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$
  D $BaO(s) + H_2O(l) \rightleftharpoons Ba^{2+}(aq) + 2OH^-(aq)$

18.2 Calculations involving acids and bases

Understandings:

• The expression for the dissociation constant of a weak acid (K_a) and a weak base (K_b).
• For a conjugate acid–base pair, $K_a \times K_b = K_w$.

  Guidance
  • *The value K_w depends on the temperature.*
  • *Only examples involving the transfer of one proton will be assessed.*
  • *Calculations of pH at temperatures other than 298 K can be assessed.*

• The relationship between K_a and pK_a is pK_a = −log K_a and between K_b and pK_b is pK_b = −log K_b.

Applications and skills:

- Solution of problems involving [H⁺(aq)], [OH⁻(aq)], pH, pOH, K_a, pK_a, K_b, and pK_b.

  Guidance
  - *Students should state when approximations are used in equilibrium calculations.*
  - *The use of quadratic equations will not be assessed.*

- Discussion of the relative strengths of acids and bases using values of K_a, pK_a, K_b, and pK_b.

  Guidance
  The calculation of pH in buffer solutions will only be assessed in options B.7 and D.4.

We have learned that acids and bases differ in their strength according to the equilibrium position of their ionization reactions. They can also be prepared in different concentrations of aqueous solution according to the ratio of acid or base to water used. Both these factors, strength and concentration, influence the pH of a solution. In this section we will learn how to quantify these relationships.

K_w is temperature dependent

The ionic product constant of water, K_w, was derived on pages 358–359.

$$K_w = [H^+][OH^-] = 1.00 \times 10^{-14} \text{ at } 298 \text{ K}$$

As K_w is an equilibrium constant, its value must be temperature dependent. The reaction for the dissociation of water is endothermic (it involves bond breaking) and so, as we learned in Chapter 7, an increase in temperature will shift the equilibrium to the right and increase the value of K_w. This represents an increase in the concentrations of H⁺(aq) and OH⁻(aq), and so a decrease in pH. Conversely, a reduction in temperature, through its effect on shifting the equilibrium to the left, decreases the value of K_w, representing lower ion concentrations and so higher pH values. Some data to illustrate these trends are given in the table below.

Temperature / °C	K_w	[H⁺] in pure water ($\sqrt{K_w}$)	pH of pure water ($-\log_{10}[H^+]$)
0	1.5×10^{-15}	0.39×10^{-7}	7.47
10	3.0×10^{-15}	0.55×10^{-7}	7.27
20	6.8×10^{-15}	0.82×10^{-7}	7.08
25	1.0×10^{-14}	1.00×10^{-7}	7.00
30	1.5×10^{-14}	1.22×10^{-7}	6.92
40	3.0×10^{-14}	1.73×10^{-7}	6.77
50	5.5×10^{-14}	2.35×10^{-7}	6.63

In other words, the pH of pure water is 7.00 only when the temperature is 298 K. Note that at temperatures above and below this, despite changes in the pH value, water is still a neutral substance as its H⁺(aq) concentration is equal to its OH⁻(aq) concentration. It does not become acidic or basic as we heat it and cool it respectively!

The temperature dependence of K_w means that the temperature should always be stated alongside pH measurements.

TOK Because many people are so familiar with the value 7.00 as the pH of water, it is often more difficult to convince them that water with a pH of greater or less than this is still neutral. Can you think of other examples where entrenched prior knowledge might hinder a fuller understanding of new knowledge? Are we likely to misinterpret experimental data when it does not fit with our expectations based on prior knowledge?

pH and pOH scales are inter-related

In section 8.3 we learned that the pH scale was introduced in order to simplify the expression of the H^+ concentration in a solution, and in particular it helps us to compare different solutions in terms of their H^+ content. The same rationale can be applied to the OH^- ions. Like H^+ ions, OH^- ions are often present in low concentrations in solutions and so have negative exponents when expressed as mol dm^{-3} that can be awkward to work with. The parallel scale, known as the **pOH scale**, is therefore used to describe the OH^- content of solutions.

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

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

As explained on page 356, the logarithmic nature of these scales means that a change of one unit in pH or pOH represents a 10× change in $[H^+]$ or $[OH^-]$ respectively. The scales are inverse, so the higher the H^+ or OH^- concentration, the smaller the pH or pOH value. These values are usually positive and have no units.

In all aqueous solutions at 298 K: pH + pOH = 14

From the relationship $[H^+][OH^-] = K_w = 1.00 \times 10^{-14}$ at 298 K, it follows that

$$10^{-pH} \times 10^{-pOH} = 1.00 \times 10^{-14} \text{ at 298 K}$$

By taking the negative logarithm to base 10 of both sides, we get

$$pH + pOH = 14.00 \text{ at 298 K}$$

The relationships between pH, $[H^+]$, pOH, and $[OH^-]$ are shown in Figure 8.8.

Figure 8.8 Relationship between $[H^+]$, $[OH^-]$, pH, and pOH at 298 K.
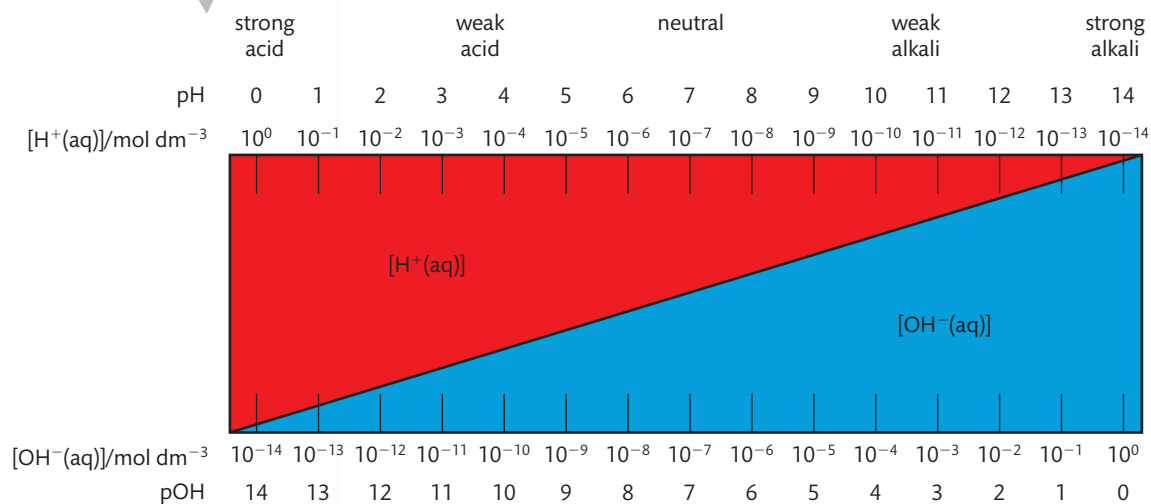
In the same way as the negative logarithms to base 10 of H^+ and OH^- are known as pH and pOH respectively, the same terminology can be applied to K_w to derive **pK_w**.

- $pK_w = -\log_{10}(K_w)$
- $K_w = 10^{-pK_w}$

pH + pOH = pK_w

So we can rewrite the expression above in a form that will apply to all temperatures:

$$pH + pOH = pK_w$$

Summary of the relationships between [H⁺], [OH⁻], pH, and pOH

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

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

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

pH $\quad\longrightarrow\quad$ H⁺(aq) $\quad\longrightarrow\quad$ OH⁻(aq) $\quad\longrightarrow\quad$ pOH

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

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

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

$$pH + pOH = pK_w$$

Converting H⁺ and OH⁻ into pH and pOH

Many calculations on acids and bases involve inter-conversions of [H⁺] and pH, as we saw in section 8.3, and we can extend these now to include [OH⁻] and pOH.

Worked example

Lemon juice has a pH of 2.90 at 25 °C. Calculate its [H⁺], [OH⁻], and pOH.

Solution

$$[H^+] = 10^{-pH} = 10^{-2.90} = 1.3 \times 10^{-3}\ \text{mol dm}^{-3}$$

pH + pOH = 14.00 at 298 K, so pOH = 14.00 − 2.90 = 11.10

$$[OH^-] = 10^{-pOH} = 10^{-11.10} = 7.7 \times 10^{-12}\ \text{mol dm}^{-3}$$

or $K_w = [H^+][OH^-]$ so $1.00 \times 10^{-14} = (1.3 \times 10^{-3}) \times [OH^-]$

$$[OH^-] = 7.7 \times 10^{-12}\ \text{mol dm}^{-3}$$

Household products containing acids, alongside sulfuric acid. Malt vinegar contains ethanoic acid, orange juice and lemons contain citric acid, and automobile batteries usually contain sulfuric acid.

Strong acids and bases: pH and pOH can be deduced from their concentrations

We assume full dissociation for strong acids and bases. Because of this we can deduce the ion concentrations and so calculate the pH or pOH directly from the initial concentration of the solution. Note that the pH and pOH are derived from the *equilibrium* concentrations of H⁺ and OH⁻. In these examples we will use the same notation as in Chapter 7, black for data that are given in the questions and blue for derived data.

Worked example

Calculate the pH of the following at 298 K:

(a) 0.10 mol dm⁻³ NaOH(aq)

(b) 0.15 mol dm⁻³ H₂SO₄(aq)

Solution

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

initial (mol dm⁻³)   0.10

equilibrium (mol dm⁻³)   0.10
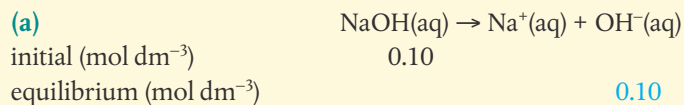
pOH = $-\log_{10}$ (0.10) = 1.0, therefore pH = 13.0

(b) $H_2SO_4(aq) \rightarrow 2H^+(aq) + SO_4^{2-}(aq)$

initial (mol dm⁻³)   0.15

equilibrium (mol dm⁻³)   0.30
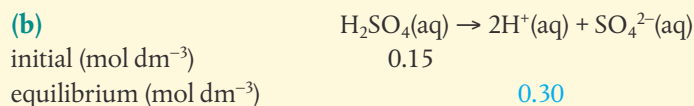
pH = $-\log_{10}$ (0.30) = 0.52

Exercises

22 At the temperature of the human body, 37 °C, the value of K_w = 2.4 × 10⁻¹⁴.

Calculate [H⁺], [OH⁻], pH, pOH, and pK_w of water at this temperature. Is it acidic, basic, or neutral?

23 The pH of a sample of milk is 6.77 at 298 K. Calculate its pOH, [H⁺], and [OH⁻]. Deduce whether it is acidic, basic, or neutral.

24 Calculate the pH of the following solutions:

(a) 0.40 mol dm⁻³ HCl

(b) 3.7 × 10⁻⁴ mol dm⁻³ KOH

(c) 5.0 × 10⁻⁵ mol dm⁻³ Ba(OH)₂

25 Which values are correct for a solution of NaOH of concentration 0.010 mol dm⁻³ at 298 K?

A [H⁺] = 1.0 × 10⁻² mol dm⁻³ and pH = 2.00

B [OH⁻] = 1.0 × 10⁻² mol dm⁻³ and pH = 12.00

C [H⁺] = 1.0 × 10⁻¹² mol dm⁻³ and pOH = 12.00

D [OH⁻] = 1.0 × 10⁻¹² mol dm⁻³ and pOH = 2.00

Dissociation constants express the strength of weak acids and bases

Weak acids and bases, unlike strong acids and bases, do not dissociate fully. This means we *cannot* deduce the concentrations of ions in their solutions from the initial concentrations, as the ion concentrations will depend on the extent of dissociation that has occurred. So we need some means of quantifying the extent of dissociation – and the process takes us back to equilibrium considerations.

The dissociation reactions of weak acids and weak bases can be represented as equilibrium expressions, each with their own equilibrium constant. The value of this constant will convey information about the position of equilibrium, and therefore on the extent of dissociation of the acid or base.

Consider the generic weak acid HA dissociating in water:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$
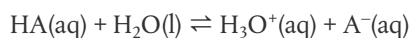
$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

Given that the concentration of water is considered to be a constant, we can combine this with K_c to produce a modified equilibrium constant known as K_a.

$$K_c[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

Therefore $K_a = \dfrac{[H_3O^+][A^-]}{[HA]}$

K_a is known as the **acid dissociation constant**. It will have a fixed value for a particular acid at a specified temperature.

As the value of K_a depends on the position of the equilibrium of acid dissociation, it gives a direct measure of the strength of an acid. *The higher the value of K_a at a particular temperature, the greater the dissociation, and so the stronger the acid.* Note that because K_a is an equilibrium constant, its value does not depend on the concentration of the acid or on the presence of other ions. We will return to this point in our study of buffer solutions in section 18.3 (page 378).

Similarly, we can consider the ionization of a base using the generic weak base B.

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$
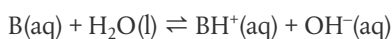
$$K_c = \frac{[BH^+][OH^-]}{[B][H_2O]}$$

Again we can combine the constants to give a modified equilibrium constant K_b.

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

Therefore $K_b = \dfrac{[BH^+][OH^-]}{[B]}$

K_b is known as the **base dissociation constant**. It will have a fixed value for a particular base at a specified temperature.

As with K_a, the value of K_b relates to the position of the equilibrium and so in this case to the strength of the base. *The higher the value of K_b at a particular temperature, the greater the ionization and so the stronger the base.*
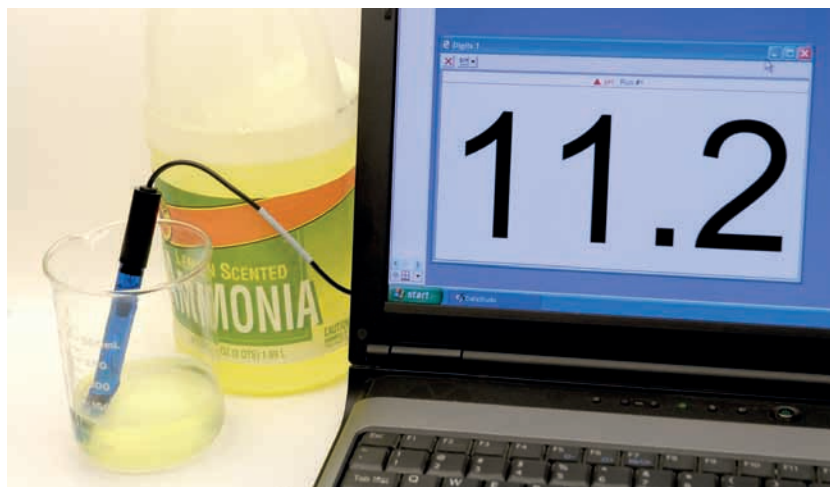
! Note that the term **acid dissociation constant** is sometimes used interchangeably with the term **acid ionization constant**. You should be comfortable to recognize either terminology in textbooks and questions.
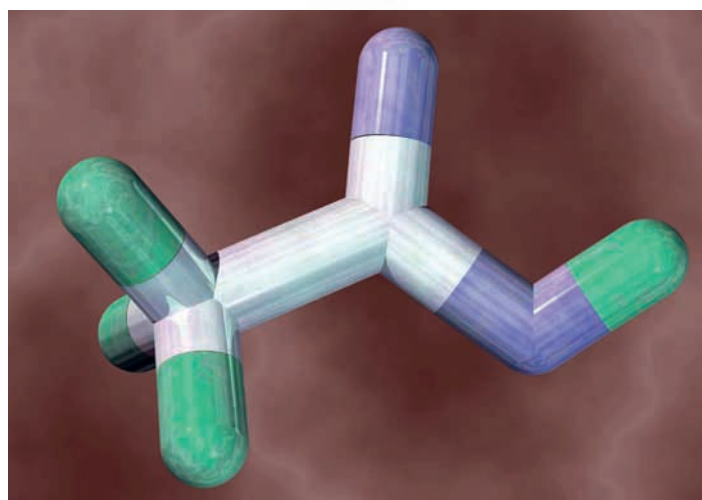
▲ Computer model of a molecule of ethanoic acid, CH_3COOH. The atoms (tubes) are colour coded: carbon is white, hydrogen is green, and oxygen is purple. Ethanoic acid is a weak acid, and is used in many of the examples in this chapter. It is used in the production of plastics and also as a preservative.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

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

The values of K_a and K_b are constant for a specific acid and base respectively, at a specified temperature. Their values give a measure of the strength of the acid or base.

A pH probe interfaced to a computer showing ammonia solution to have a pH of 11.2. It is a weak base, used in many of the examples in this chapter.
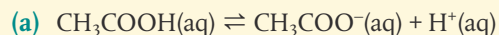
Worked example

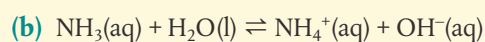Write the expressions for K_a and K_b for the following acid and base.

(a) $CH_3COOH(aq)$

(b) $NH_3(aq)$
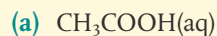
Solution

First write the equation for the equilibrium reactions – remembering that acids donate H^+ and bases accept H^+.

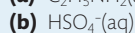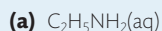**(a)** $CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

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

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

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

Exercises

26 Write the expressions for K_b for the following:

    (a) $C_2H_5NH_2(aq)$
    (b) $HSO_4^-(aq)$
    (c) $CO_3^{2-}(aq)$

27 Place the following acids in order of increasing strength.

    H_3PO_4 $K_a = 7.1 \times 10^{-3}$
    HNO_2 $K_a = 7.1 \times 10^{-4}$
    H_2SO_3 $K_a = 1.2 \times 10^{-2}$
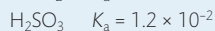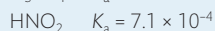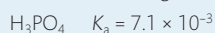
28 Why do you think we do not usually use the concept of K_a and K_b to describe the strength of strong acids and bases?

Calculations involving K_a and K_b

The values of K_a and K_b enable us to compare the strengths of weak acids and bases, and to calculate ion concentrations present at equilibrium and so the pH and pOH values. Examples of these calculations are given below. Note that many of these questions are approached in a similar manner to those given in Chapter 7. It is assumed here that you are familiar with that work, so it may be useful for you to refresh your memory of section 17.1 before continuing.

The following points are to remind you of some key points and guide you in all the calculations that follow:

• The given concentration of an acid or base is its *initial* concentration – before dissociation occurs.

• The pH (or pOH) of a solution refers to the concentration of H^+ ions (or OH^- ions) at *equilibrium*.

• The concentration values substituted into the expressions for K_a and K_b must be the *equilibrium* values for all reactants and products.

• When the extent of dissociation is very small (very low value for K_a or K_b) it is appropriate to use the approximations:

$$[acid]_{initial} \approx [acid]_{equilibrium}$$

$$[base]_{initial} \approx [base]_{equilibrium}$$

Make sure you clearly state when an approximation is made in a calculation, and justify it in terms of the small value of K.

1 Calculation of K_a and K_b from pH and initial concentration

Worked example

Calculate K_a at 298 K for a 0.01 mol dm^{-3} solution of ethanoic acid (CH_3COOH). It has a pH of 3.4 at this temperature.

Solution

Write the equation for the dissociation of the acid. Insert the data in three rows: initial, change, and equilibrium. As in Chapter 7, numbers in black are data that were given in the question, numbers in blue have been derived.

From the pH we get the [H$^+$] at equilibrium:

pH 3.4 $\Rightarrow$ [H$^+$] = $10^{-3.4}$ = 4.0×10^{-4} mol dm^{-3}

From the stoichiometry of the reaction we know that [H$^+$] = [CH$_3$COO$^-$]

	$CH_3COOH(aq)$	$\rightleftharpoons$	$CH_3COO^-(aq)$ +	$H^+(aq)$
initial (mol dm^{-3})	0.01		0.00	0.00
change (mol dm^{-3})	-4×10^{-4}		$+4 \times 10^{-4}$	$+4 \times 10^{-4}$
equilibrium (mol dm^{-3})	$0.01 - (4 \times 10^{-4})$		4×10^{-4}	4×10^{-4}
	~ 0.01			

The approximation $0.01 \approx 0.01 - (4 \times 10^{-4})$ is valid within the precision of this data.

Write the expression for K_a and substitute the equilibrium values.

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{(4 \times 10^{-4})^2}{0.01} = 1.6 \times 10^{-5}$$

Worked example

Calculate the K_b for a 0.100 mol dm^{-3} solution of methylamine, CH_3NH_2 at 25 °C. Its pH is 11.80 at this temperature.

Solution

At 25 °C (298 K), pH + pOH = 14.00. Therefore pH 11.80 $\Rightarrow$ pOH = 2.20

[OH$^-$] = 10^{-pOH} = $10^{-2.20}$ = 6.3×10^{-3}

From the stoichiometry of the reaction [OH$^-$] = [CH$_3$NH$_3^+$]

	$CH_3NH_2(aq)$ +	$H_2O(l)$	$\rightleftharpoons$	$CH_3NH_3^+(aq)$ +	$OH^-(aq)$
initial (mol dm^{-3})	0.100			0.000	0.000
change (mol dm^{-3})	-0.00630			$+0.00630$	$+0.00630$
equilibrium (mol dm^{-3})	0.0937			0.00630	0.00630

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} = \frac{(0.00630)^2}{0.0937} = 4.22 \times 10^{-4}$$

2 Calculation of [H⁺] and pH, [OH⁻] and pOH from K_a and K_b

Worked example

A 0.75 mol dm⁻³ solution of ethanoic acid has a value for $K_a = 1.8 \times 10^{-5}$ at a specified temperature. What is its pH at this temperature?

Solution

To calculate pH we need to know [H⁺] at equilibrium, and therefore the amount of dissociation of the acid that has occurred: this is the 'change' amount in the reaction.

So let the change in concentration of $CH_3COOH = -x$

Therefore change in concentration of CH_3COO^- and $H^+ = +x$

	$CH_3COOH(aq)$	$\rightleftharpoons$ $CH_3COO^-(aq)$	+ $H^+(aq)$
initial (mol dm⁻³)	0.75	0.00	0.00
change (mol dm⁻³)	$-x$	$+x$	$+x$
equilibrium (mol dm⁻³)	$0.75 - x$	x	x
	~ 0.75		

As K_a is very small, x, the amount of dissociation, is also extremely small and it is valid to approximate $[CH_3COOH]_{initial} \approx [CH_3COOH]_{equilibrium}$.

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{x^2}{0.75} = 1.8 \times 10^{-5}$$

Therefore $x = \sqrt{1.8 \times 10^{-5} \times 0.75} = 3.7 \times 10^{-3}$

$[H^+] = 3.7 \times 10^{-3} \Rightarrow pH = 2.4$

Worked example

A 0.20 mol dm⁻³ aqueous solution of ammonia has K_b of 1.8×10^{-5} at 298 K. What is its pH?

Solution

Let the change in concentration of $NH_3 = -x$

Therefore change in concentration of NH_4^+ and $OH^- = +x$

	$NH_3(aq)$ + $H_2O(l)$	$\rightleftharpoons$ $NH_4^+(aq)$	+ $OH^-(aq)$
initial (mol dm⁻³)	0.20	0.00	0.00
change (mol dm⁻³)	$-x$	$+x$	$+x$
equilibrium (mol dm⁻³)	$0.20 - x$	x	x
	≈ 0.20		

As K_b is very small, x the amount of dissociation is also extremely small, and so it is valid to approximate $[NH_3]_{initial} \approx [NH_3]_{equilibrium}$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{0.20} = 1.8 \times 10^{-5}$$

Therefore $x = \sqrt{1.8 \times 10^{-5} \times 0.20} = 1.9 \times 10^{-3}$

$[OH^-] = 1.9 \times 10^{-3}$

$pOH = -\log_{10}(1.9 \times 10^{-3}) = 2.72$

Therefore at 298 K, pH = $14.00 - 2.72 = 11.28$

Exercises

29 The acid dissociation constant of a weak acid has a value of 1.0×10^{-5} mol dm^{-3}. What is the pH of a 0.1 mol dm^{-3} aqueous solution of HA?

    A 2   **B** 3   **C** 5   **D** 6

30 Calculate the K_b of ethylamine, $C_2H_5NH_2$, given that a 0.10 mol dm^{-3} solution has a pH of 11.86.

31 What are the [H$^+$] and [OH$^-$] in a 0.10 mol dm^{-3} solution of an acid that has $K_a = 1.0 \times 10^{-7}$?

pK_a and pK_b

We have seen that K_a and K_b values give us a direct measure of the relative strengths of weak acids and bases. But as these values are characteristically very small, they usually involve dealing with numbers with negative exponents, which we have acknowledged before are clumsy to use as the basis for comparisons. They also span a wide range of values. So, in the same way as with the concentrations of H$^+$ and OH$^-$ ions and K_w, and for the same reason, we can convert K_a and K_b values into their negative logarithms to the base 10, known as **pK_a** and **pK_b**.

- pK_a = $-\log_{10} K_a$;
- $K_a = 10^{-\text{p}K_a}$

- pK_b = $-\log_{10} K_b$;
- $K_b = 10^{-\text{p}K_b}$

Some examples of K_a and pK_a, K_b and pK_b values are given below, all at 298 K.

Acid	Formula	K_a	pK_a
methanoic	HCOOH	1.8×10^{-4}	3.75
ethanoic	CH$_3$COOH	1.8×10^{-5}	4.76
propanoic	C$_2$H$_5$COOH	1.4×10^{-5}	4.87

Base	Formula	K_b	pK_b
ammonia	NH$_3$	1.8×10^{-5}	4.75
methylamine	CH$_3$NH$_2$	4.6×10^{-4}	3.34
ethylamine	C$_2$H$_5$NH$_2$	4.5×10^{-4}	3.35

The following points follow from the table.

1   pK_a and pK_b numbers are usually positive and have no units.

Although the derivation of K_a and K_b can be applied to any acid or base, it is really useful mostly for weak acids and bases where the extent of dissociation is small. The fact that these have negative powers means that their pK_a and pK_b values will be positive, as we can see in the examples in the table above.

2   The relationship between K_a and pK_a and between K_b and pK_b is inverse.

Stronger acids or bases with higher values for K_a or K_b have lower values for pK_a or pK_b.

<div align="center">

STRONG ACID   **STRONG BASE**

K_a increases   pK_a increases K_b increases   pK_b increases

WEAK ACID   **WEAK BASE**

</div>

▲ Stinging nettle plants. The leaves are covered in sharp hairs which when touched inject a painful mixture of chemicals including the weak acid methanoic acid HCOOH into the skin. The stinging sensation can be relieved by rubbing the skin with leaves of a plant such as dock, which has a mildly basic sap and so helps to neutralize the acid.

CHALLENGE YOURSELF

1 In organic acids and bases, increasing the length of the carbon chain *decreases* the acid strength of the –COOH group but *increases* the basic strength of $C_2H_5NH_2$ relative to CH_3NH_2. Can you suggest why this is so? Hint: think about the electron density distributions in the molecules.

3 A change of one unit in pK_a or pK_b represents a 10 fold change in the value of K_a or K_b.

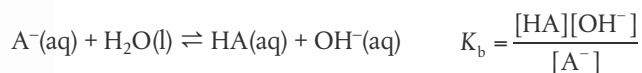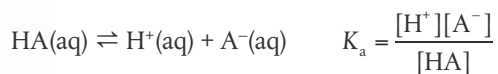This is because the scale is logarithmic to base 10.

4 pK_a and pK_b must be quoted at a specified temperature.

This is because the values are derived from the temperature-dependent constants, K_a and K_b.

Table 21 in the IB data booklet gives pK_a and pK_b values for a range of common weak acids and bases. These are the data commonly quoted to describe acid and base strengths, so in calculation questions you may first need to convert pK_a and pK_b into K_a or K_b values. This is done by taking anti-logarithms, as we did with pH, pOH, and pK_w.

Relationship between K_a and K_b, pK_a and pK_b for a conjugate pair

Consider the K_a and K_b expressions for a conjugate acid–base pair HA and A^-.

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

$$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq) \qquad K_b = \frac{[HA][OH^-]}{[A^-]}$$

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

Therefore $K_a \times K_b = [H^+] \times [OH^-] = K_w$

By taking negative logarithms of both sides:

$pK_a + pK_b = pK_w$

At 298 K, $K_w = 1.00 \times 10^{-14}$ so $pK_w = 14.00$

Therefore $pK_a + pK_b = 14.00$ at 298 K

This relationship holds for any conjugate acid–base pair in aqueous solution, so from the value of K_a of the acid we can calculate K_b for its conjugate base. It shows that the higher the value of K_a for the acid, the lower the value of K_b for its conjugate base. In other words, stronger acids have weaker conjugate bases, and vice versa. This gives a quantitative basis for the relative strengths of conjugate acid–base pairs, discussed qualitatively on page 361. It makes sense in the context of equilibrium positions. For a conjugate pair such as

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$
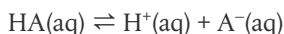
the weaker the acid HA, the further this equilibrium lies to the left; this means the stronger the base A^-, the greater its tendency to accept the proton. So acids and bases react to form the weaker conjugate, as illustrated in Figure 8.9.

For any conjugate acid–base pair:

- $K_a \times K_b = K_w$
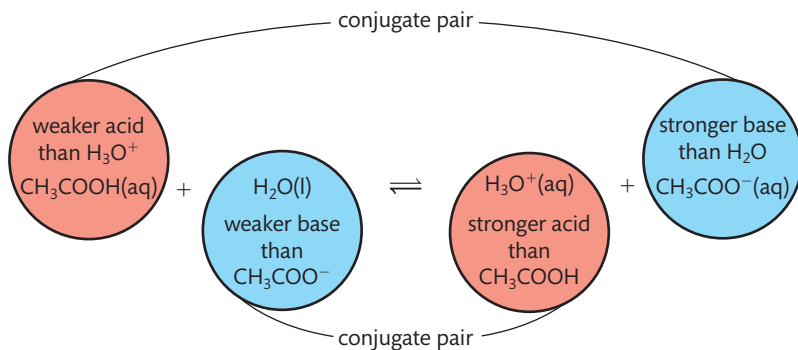- $pK_a + pK_b = pK_w$
- $pK_a + pK_b = 14$ at 298 K

Figure 8.9 The reaction between CH₃COOH and H₂O. At equilibrium the mixture lies in favour of the weaker conjugates, the acid CH₃COOH and the base H₂O.

The inverse relationship between the strengths of acids and their conjugate bases is shown in Figure 8.10.

Figure 8.10 The relative strengths of some acids and their conjugate bases in aqueous solution.

NATURE OF SCIENCE

The application of the equilibrium law to acid–base equilibria leads to a number of different derived equilibrium constants. These can be used to solve a wide range of numerical problems, which allow the strength of acids and bases to be determined. Explanation of patterns and trends in the relative strengths of acids and bases is based on interpretations of their molecular structures. This flow of understanding and knowledge across a range of phenomena is central to the study of chemistry.

Exercises

32 A weak acid HA has a pK_a of 4.92. What will be the [H⁺] and pH of a 0.030 mol dm⁻³ solution of this acid?

33 What is the relationship between K_a and pK_a?

   A   pK_a = −log K_a

   B   p$K_a = \dfrac{1.0 \times 10^{-14}}{K_a}$

   C   pK_a = log K_a

   D   p$K_a = \dfrac{1.0}{K_a}$

34 The pK_a of HCN is 9.21 and that of HF is 3.17. Which is the stronger acid?

35 Look at the data in Q34. What are the pK_b values of CN⁻ and F⁻? Which is the stronger base?

36 (a) The pK_a of ethanoic acid, CH₃COOH, at 298 K is 4.76. What is the pK_b of its conjugate base CH₃COO⁻?

   (b) The pK_a of methanoic acid, HCOOH, at 298 K is 3.75. Is its conjugate base weaker or stronger than that of ethanoic acid?

18.3 pH curves

Buffer solutions

A buffer refers to something that acts to reduce the impact of one thing on another – a little bit like a shock absorber. For example, buffers in the computer world are areas shared by hardware devices that operate at different speeds. In acid–base chemistry, a buffer acts to reduce the pH impact of added acid or base on a chemical system. It is defined as follows:
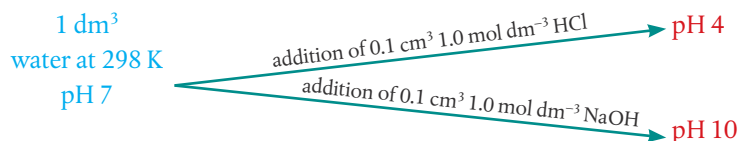
pH buffers are not the only type of buffer in physical science. Other examples include thermal buffers that help to maintain a constant temperature, and mineral redox buffers which help to stabilize oxidation states in natural rock systems. But buffering pH is by far the most common application, and so the term 'buffer' in chemistry is generally used synonymously with 'pH buffer'.

It is defined as follows:

A buffer solution is resistant to changes in pH on the addition of small amounts of acid or alkali.

To understand the importance of buffers, it is useful to see how added acid or alkali changes the pH of a non-buffered solution. This is shown below.

1 dm³
water at 298 K
pH 7

addition of 0.1 cm³ 1.0 mol dm⁻³ HCl → **pH 4**

addition of 0.1 cm³ 1.0 mol dm⁻³ NaOH → **pH 10**

Note the volume added here is merely 0.1 cm³ – just a few drops. Evidently, water is very vulnerable to significant fluctuations in its pH and this can have major impacts on chemical reactions in aqueous solutions. However, biological systems are able to operate efficiently only within a narrow range of pH, principally because of the effect that pH change has on enzyme activity and so on all biochemical reactions. These systems are therefore dependent on buffers, and mammalian blood is an excellent example of a complex natural buffer. Ocean chemistry also includes effective buffer systems, which help to maintain the conditions suitable for life. Many chemical processes such as electrophoresis and fermentation, the dyes industry, and calibration of instruments depend on effective buffering.

Ocean water has a pH around 8–9, controlled by several buffer systems. The carbonate and hydrogencarbonate ions, existing in equilibrium: $CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$, are crucial to the buffering action. The ocean has the capacity to absorb huge amounts of CO_2 from the atmosphere, so acts as a CO_2 'sink', which is very important in helping to alleviate the effects of increasing atmospheric CO_2. But as CO_2 dissolves in the ocean, it makes the water more acidic, releasing H^+ that shifts the equilibrium and reduces the concentration of CO_3^{2-}. Coral reefs are directly affected by this, as they depend on the carbonate ion to build their structures, and have shown serious decline with decreasing carbonate levels. Of potentially greater impact still is the fact that the decrease in pH of the water may set up a feedback loop, reducing the ocean's buffering capacity and so diminish its ability to take up additional CO_2 from the atmosphere. Many research scientists believe that ocean acidification is potentially the most serious of all predicted outcomes of increase in atmospheric CO_2.

When giving the definition of a buffer, be sure to include the '*small amount*' for the added acid or alkali. Otherwise you imply that buffers have infinite ability to maintain the pH, which is not the case.

Note that although buffers maintain the pH close to a set value, they do not all work at pH 7. Different buffer solutions can be made to buffer at almost any pH.

Turret coral on the Great Barrier Reef, Australia. Corals depend on carbonate ions in the ocean to build their hard structures made from calcium carbonate. In many parts of the world coral reefs are threatened by changes in the ocean chemistry, especially the loss of buffering capacity and decreasing pH that is a result of increasing atmospheric carbon dioxide.

How buffers work

There are two main types of buffer solution – acidic buffers that maintain the pH at a value less than 7 and basic buffers that maintain the pH at a value greater than 7. We will see that both are a *mixture* of two solutions, composed in such a way that they each contain the *two* species of a conjugate acid–base pair. The key to understanding their buffering action is to focus on the equilibria in the solutions and to pick out the species that respond to added H^+ and OH^-. These are shown in red below.
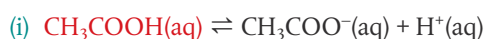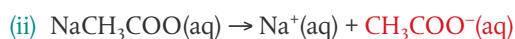
1   Acidic buffers

Composition of the buffer solution

Made by mixing an aqueous solution of a weak acid with a solution of its salt of a strong alkali. For example:

$$CH_3COOH(aq) \quad \text{and} \quad NaCH_3COO(aq)$$
<center>weak acid   salt of weak acid
with strong alkali</center>
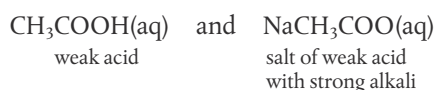
The following equilibria exist in a solution of this mixture:

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

$CH_3COOH(aq)$ is a weak acid, so equilibrium lies to the left.

(ii) $NaCH_3COO(aq) \rightarrow Na^+(aq) + CH_3COO^-(aq)$

$CH_3COO^-(aq)$ is a soluble salt, so is fully dissociated in solution.

So the mixture contains relatively high concentrations of both CH_3COOH and CH_3COO^-, that is an acid and its conjugate base. These can be considered as 'reservoirs', ready to react with added OH^- and H^+ respectively in neutralization reactions.
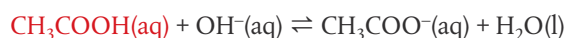
Response to added acid and base

• Addition of acid (H^+):

    H^+ will combine with the base CH_3COO^- to form CH_3COOH, therefore removing most of the added H^+.

$$CH_3COO^-(aq) + H^+(aq) \rightleftharpoons CH_3COOH(aq)$$
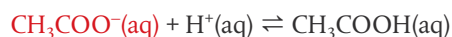
• Addition of base (OH^-):

    OH^- will combine with the acid CH_3COOH to form CH_3COO^- and H_2O, so removing most of the OH^-.

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

Consequently, as the added H^+ and OH^- are used in these reactions, they do not persist in the solution and so the pH is largely unchanged.

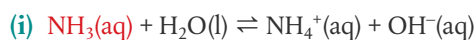### 2   Basic buffers

Composition of the buffer solution

Made by mixing an aqueous solution of a weak base with its salt of a strong acid. For example:

$$NH_3(aq) \quad \text{and} \quad NH_4Cl(aq)$$
<center>weak base   salt of weak base
with strong acid</center>
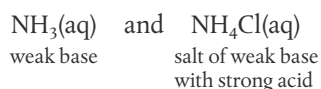
Bottle containing a buffer solution for maintaining pH at 10.00. Note the fact that this is temperature dependent. Buffers are often supplied as concentrate or as tablets and can be diluted to give a larger volume. Dilution does not change the ratio of acid to salt or base to salt so the pH remains constant whatever the volume.

Certified
**Buffer Solution
Concentrate**
For **pH 10.00**
± .02 @ 25°C.

The following equilibria exist in solution:

$$\text{(i)} \quad NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$NH_3(aq)$ is a weak base, so equilibrium lies to the left.

$$\text{(ii)} \quad NH_4Cl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

$NH_4^+(aq)$ is a soluble salt, so is fully dissociated in solution.

So here the mixture contains relatively high concentrations of both $NH_3(aq)$ and $NH_4^+(aq)$ – that is a base and its conjugate acid. These species will again act as reservoirs, ready to react with added H^+ and OH^- respectively in neutralization reactions.
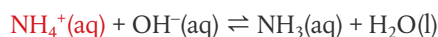
Response of buffer to added acid or alkali

• Addition of acid (H^+):

  H^+ will combine with the base NH_3 to form NH_4^+, therefore removing most of the added H^+.

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

• Addition of base (OH^-):

  OH^- will combine with the acid NH_4^+ and form NH_3 and H_2O, so removing most of the OH^-.

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

So, as with the acidic buffer, the removal of the added H^+ and OH^- by reactions with the components of the buffer solution means that they do not persist in the solution and so do not alter the pH.

In summary:

Buffer solutions are a mixture containing both an acid and a base of a weak conjugate pair. The buffer's acid neutralizes added alkali, and the buffer's base neutralizes added acid, and so pH change is resisted.

Making buffer solutions

The pH of a buffer is determined by the interactions of its components. Specifically it depends on:

1   the pK_a or pK_b of its acid or base;
2   the *ratio* of the initial concentrations of acid and salt, or base and salt, used in its preparation.

The calculation of the pH of a buffer is covered in more detail in the Biochemistry (B.7) and Medicinal chemistry (D.4) option topics in Chapters 13 and 15.

Buffer solutions can be prepared by starting with an acid or base that has a pK_a or pK_b value as close as possible to the required pH or pOH of the buffer. This is then either:

• mixed with a solution of a salt containing its conjugate or
• partially neutralized by a strong base or acid

The neutralization reaction should ensure that approximately one half of the starting acid or base is converted into salt. After reaction, the mixture will contain

A buffer solution is resistant to changes in pH on the addition of small amounts of acid or alkali.

The pH of a buffer is determined by the pK_a/pK_b of its acid/base and the ratio of its concentration of acid and salt/base and salt.

the unreacted acid or base and its salt in equimolar amounts. An example of this is illustrated below using simple mole ratios.

$$CH_3COOH(aq) + NaOH(aq) \rightarrow NaCH_3COO(aq) + H_2O(l)$$

	$CH_3COOH(aq)$	$NaOH(aq)$	$NaCH_3COO(aq)$	$H_2O(l)$
initial amounts in moles	2	1	0	0
change during reaction	−1	−1	+1	+1
final amounts in moles	1	0	1	1

The final mixture, containing equal amounts of the weak acid CH_3COOH and its salt $NaCH_3COO$, is a buffer solution.

Worked example

State whether each of the following mixtures will form a buffer solution when dissolved in 1.00 dm³ of water.

(a) 0.20 mol $NaHCO_3$ and 0.20 mol Na_2CO_3
(b) 0.20 mol CH_3COOH and 0.10 mol HCl
(c) 0.20 mol NH_3 and 0.10 mol HCl
(d) 0.10 mol H_3PO_4 and 0.20 mol NaOH

Solution

(a) Solution contains HCO_3^- and CO_3^{2-}, a conjugate pair, so it is a buffer.
(b) Solution contains two acids – it is not a buffer.
(c) NH_3 and HCl react together forming 0.10 mol NH_4Cl and 0.10 mol NH_3 unreacted; it is a buffer.
(d) H_3PO_4 and NaOH react together forming 0.20 mol Na_2HPO_4

$$H_3PO_4(aq) + 2NaOH(aq) \rightarrow Na_2HPO_4 + 2H_2O(l)$$

it is not a buffer.

Factors that can influence buffers

Now that we know what determines the pH of a buffer, we can predict how it will respond in certain situations.

1 Dilution

K_a and K_b are equilibrium constants and so are not changed by dilution. Dilution also does not change the *ratio* of acid or base to salt concentration, as both components will be decreased by the same amount. Therefore diluting a buffer does not change its pH.

Nonetheless, diluting a buffer does alter the amount of acid or base it can absorb without significant changes in pH – the so-called **buffering capacity**. This depends on the molar concentrations of its components, so decreases as they are lowered by dilution.

2 Temperature

As temperature affects the values of K_a and K_b, it does affect the pH of the buffer. This is why a constant temperature should be maintained in all work involving buffers, such as calibration of pH meters. Temperature fluctuations must also be minimized in many medical procedures such as blood transfusions, due to the effect on the buffers in the blood.

> Dilution does not change the pH of a buffer, but it lowers its buffering capacity.

CHALLENGE YOURSELF

2 Contrast and explain how the pH of each of the following types of solution responds to dilution:
(a) strong acid
(b) weak acid
(c) buffer

At high altitudes, where the air pressure and therefore the concentration of O_2 is significantly less than at sea level, some people suffer from altitude sickness. This is a potentially fatal condition that involves an increase in the pH of the blood (alkalosis). The causes are complex but stem from a decrease in CO_2 in the blood, resulting from hyperventilation. Drugs that can alleviate the symptoms lower the concentration of HCO_3^- through stimulating its excretion by the kidneys. This shifts the equilibrium:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$
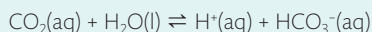
to the right and so acidifies the blood. Indigenous cultures in the Andes have used coca leaves for centuries to alleviate mild symptoms of altitude sickness, although the way in which this may be achieved is not fully understood.


Climbers in the Andes, Peru. At high altitudes like this, the lower concentration of oxygen in the air makes it more difficult to do vigorous exercise. Climbers need to acclimatize to the level of oxygen available in order to avoid problems caused by alkalosis of the blood.

Exercises

37 Which mixture would produce a buffer solution when dissolved in 1.0 dm³ of water?

    A   0.50 mol of CH_3COOH and 0.50 mol of NaOH
    B   0.50 mol of CH_3COOH and 0.25 mol of NaOH
    C   0.50 mol of CH_3COOH and 1.00 mol of NaOH
    D   0.50 mol of CH_3COOH and 0.25 mol of $Ba(OH)_2$

38 A buffer solution can be prepared by adding which of the following to 50 cm³ of 0.10 mol dm⁻³ $CH_3COOH(aq)$?

    I   50 cm³ of 0.10 mol dm⁻³ $NaCH_3COO(aq)$
    II   25 cm³ of 0.10 mol dm⁻³ NaOH(aq)
    III   50 cm³ of 0.10 mol dm⁻³ NaOH(aq)

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

39 State and explain which of the following has the greater buffering capacity:

    (i) 100 cm³ 0.30 mol dm⁻³ HNO_2 and 0.30 mol dm⁻³ $NaNO_2$ or
    (ii) 100 cm³ 0.10 mol dm⁻³ HNO_2 and 0.10 mol dm⁻³ $NaNO_2$.

Salt hydrolysis

We saw on page 351 that a neutralization reaction between an acid and a base produces a salt – an ionic compound containing a cation from the parent base and an anion from the parent acid. The cation is the conjugate acid of the parent base and the anion is the conjugate base of the parent acid.

<div align="center">

parent base + parent acid → salt + water

MOH   HA M^+A^- H_2O

</div>
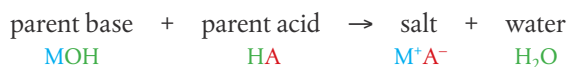
But although salts are the products of a neutralization reaction, they do not all form neutral aqueous solutions. Their pH in solution depends on whether and to what

extent their ions, which are conjugate acids and bases, react with water and hydrolyse it, releasing H^+ or OH^- ions. Remember in section 18.2 we showed through pK_a and pK_b values that the weaker the acid or base the stronger its conjugates, and vice versa. The relative strengths of the conjugate acids and bases in the salt determines the extent of hydrolysis reactions and so the pH of the salt solution.
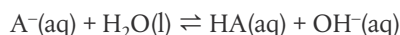
Salt of strong acid and strong base – no hydrolysis

The reaction between a strong acid and a strong base forms a salt in which both the conjugate acid and the conjugate base are weak. As a result there is virtually no hydrolysis of ions, and the pH is close to neutral. For example:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

pH approximately 7
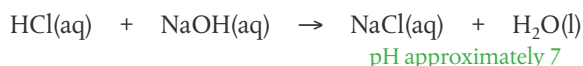
Solutions of salts of strong acids with strong bases have a pH ≈ 7 at 298 K.
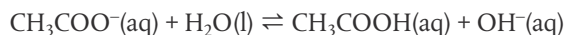
Salt of weak acid and strong base – anion hydrolysis

The anion (A^-) is a conjugate base of the parent acid. When the acid is weak this conjugate base is strong enough to cause hydrolysis:

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

The release of OH^- causes the pH of the solution to *increase*.

For example, the salt $NaCH_3COO$, containing the conjugate base CH_3COO^-, causes hydrolysis:

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

Solutions of salts of weak acids with strong bases have a pH > 7 at 298 K.
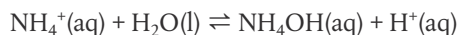
Salt of strong acid and weak base – cation hydrolysis

The cation (M^+) is a conjugate of the parent base. When the base is weak and this conjugate is a non-metal (e.g. NH_4^+), it is able to hydrolyse water:

$$M^+(aq) + H_2O(l) \rightleftharpoons MOH(aq) + H^+(aq)$$
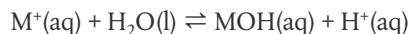
The release of H^+ causes the pH of the solution to *decrease*.

For example:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_4OH(aq) + H^+(aq)$$

Solutions of salts of strong acids with weak bases have a pH < 7 at 298 K.

When the cation is a metal ion, the situation is a little more complex as it depends on the metal's charge density. Metal ions that have a high charge density, such as Al^{3+} and Fe^{3+}, carry out hydrolysis, releasing H^+ from water. As a result they form acidic solutions.

Salt of weak acid and weak base

When a weak acid reacts with a weak base, they form a salt in which both the conjugates are relatively strong and carry out hydrolysis. The pH of the solution therefore depends on the relative K_a and K_b values of the acids and bases involved.

Salts of strong acids and strong bases are neutral.

Salts of weak acids and strong bases are basic.

Salts of strong acids and weak bases are acidic.

Summary

The pH of a salt solution depends on the relative hydrolysis of its anions and cations, which can be deduced from the relative strengths of the parent acids and bases. The table below summarizes this.

Neutralization reaction	Example of parent acid and base	Salt formed	Hydrolysis of ions	Type of salt solution	pH of salt solution
strong acid and strong base	$HCl(aq) + NaOH(aq)$	$NaCl(aq)$	neither ion hydrolyses	neutral	7
weak acid and strong base	$CH_3COOH(aq) + NaOH(aq)$	$NaCH_3COO(aq)$	anion hydrolyses	basic	>7
strong acid and weak base	$HCl(aq) + NH_3(aq)$	$NH_4Cl(aq)$	cation hydrolyses	acidic	<7
weak acid and weak base	$CH_3COOH(aq) + NH_3(aq)$	$NH_4CH_3COO(aq)$	anion and cation hydrolyse	depends on relative strengths of conjugates	cannot generalize

Exercises

40 Predict for each salt in aqueous solution whether the pH will be greater than, less than, or equal to 7.

(a) NaCl
(b) $FeCl_3$
(c) NH_4NO_3
(d) Na_2CO_3

41 Which compound will dissolve in water to give a solution with a pH greater than 7?

A   sodium chloride
B   potassium carbonate
C   ammonium nitrate
D   lithium sulfate

42 Deduce whether the pH of the resulting salt solution will be greater than, less than, or equal to 7 when the following solutions exactly neutralize each other.

(a) $H_2SO_4(aq) + NH_3(aq)$
(b) $H_3PO_4(aq) + KOH(aq)$
(c) $HNO_3(aq) + Ba(OH)_2(aq)$

Acid–base titrations

The neutralization reactions between acids and bases described above can be investigated quantitatively using titration, as introduced in section 8.2. Titration is one of the most widely used procedures in chemistry. Quality control of food and drink production, health and safety checks in the cosmetic industry, and clinical analysis in medical services are just some examples of its use.

Controlled volumes of one reactant are added from a **burette** to a fixed volume of the other reactant that has been carefully measured using a **pipette** and placed in a conical flask. The reaction between acid and base takes place in the flask until the **equivalence point** or **stoichiometric point** is reached, where they exactly neutralize each other. An indicator or a pH meter are used to detect the exact volume needed to reach equivalence.

Addition of base from the burette to an acid in the conical flask containing ▶ phenolphthalein indicator. As the neutralization reaction happens, the change in the pH of the reaction mixture causes a change in the colour of the indicator. Drop-wise addition of the base ensures that an accurate measure of the equivalence point can be made.

When a base is added to an acid in the neutralization reaction, there is a change in pH as we would expect. But this change does not show a linear relationship with the volume of base added, partly due to the logarithmic nature of the pH scale. The easiest way to follow the reaction is to record pH using a pH meter or data-logging device as a function of volume of base added, and plot these values as **pH curves**.

pH curves can also be derived from theory – by calculating the pH at different volumes of base added. The process is a lot more laborious but produces the same results. Some sample calculations for the first titration discussed (strong acid–strong base) are given here to illustrate how this is done. Similar calculations based on the processes used earlier in this chapter can be done for the other three reactions.

It is found that in most titrations a big jump in pH occurs at equivalence, and this is known as the **point of inflection**. The equivalence point is determined as being half-way up this jump.

We will consider all four combinations of strong and weak acid and base here, and will see that the pH curves have specific features that relate to the strengths of the acid and base. To make comparisons of the curves easier, these examples all use:

- 0.10 mol dm^{-3} solutions of all acids and bases;
- an initial volume of 50.0 cm^3 of acid in the conical flask with base added from the burette;
- acids and bases which all react in a 1 : 1 ratio, so that equivalence is achieved at equal volumes for these equimolar solutions (i.e. when 50 cm^3 of base has been added to the 50 cm^3 of acid).

At the equivalence point, the acid and base have exactly neutralized each other, so the solution contains salt and water only. Remember that the pH of this solution depends on hydrolysis by ions in the salt, determined by the relative strengths of the parent acid and base – as explained on pages 384–385.

> The equivalence point occurs when stoichiometrically equivalent amounts of acid and base have reacted together. At this point the solution contains salt and water only.

1 Strong acid and strong base

For example:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$
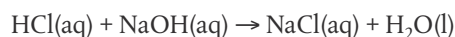
- pH at equivalence = 7 as neither ion hydrolyses appreciably.

The calculations in the section below are a sample to show the reasons for the shape of the pH curve. In this example we assume full dissociation because these are strong acids and bases. Note also that as the base is added to the acid, neutralization of some of the acid occurs, while excess acid remains – until equivalence where the amounts of acid and base have fully reacted. After equivalence the mixture contains excess base. As the volume changes during the addition, this must be taken into account in determining the concentrations.

As the volume of base added increases, we can see how the resulting pH changes.

Volume of base added				
0.00 cm³ (flask contains acid only)	25.00 cm³	49.00 cm³	50.00 cm³ (contents of flask at equivalence)	51.00 cm³ (flask contains excess base)
	(flask contains excess acid)			
$[acid]_{initial}$ = 0.10 mol dm⁻³ $[H^+] = 1 \times 10^{-1}$ **pH = 1.0**	$n(acid\ initial) = cV = 0.10 \times 0.050 = 0.0050$ mol $n(base\ added) = cV = 0.10 \times 0.0250 = 0.00250$ mol $n(acid\ remaining) = 0.0050 - 0.00250 = 0.00250$ $n(H^+) = 0.00250$ mol new volume = 0.0750 dm³ so $[H^+] = 0.0333$ **pH = 1.5**	$n(acid\ initial) = 0.0050$ mol $n(base\ added) = cV = 0.10 \times 0.0490 = 0.00490$ $n(acid\ remaining) = 0.0050 - 0.00490 = 0.00010$ mol $n(H^+) = 0.00010$ mol new volume = 0.0990 dm³ so $[H^+] = 0.00101$ **pH = 3.0**	All of the acid has been neutralized by the base; the solution contains $NaCl + H_2O$ only **pH = 7.0**	$n(base\ added) = cV = 0.10 \times 0.0510 = 0.00510$ $n(base\ remaining) = 0.00510 - 0.0050 = 0.00010$ $n(OH^-) = 0.00010$ mol new volume = 0.101 dm³ so $[OH^-] = 0.00099$ so pOH = 3 **pH = 11.0**

These calculations show that the initial pH is low as this is a strong acid. As base is added, the increase in pH is at first very gradual, so that even when the mixture is only 1.0 cm³ away from equivalence it is still a long way below pH 7. A small addition of base around the equivalence point causes a dramatic rise in pH, with an increase of about eight units from pH 3 to 11.

The pH curve showing these pH changes over the full range of addition of base is shown in Figure 8.11.
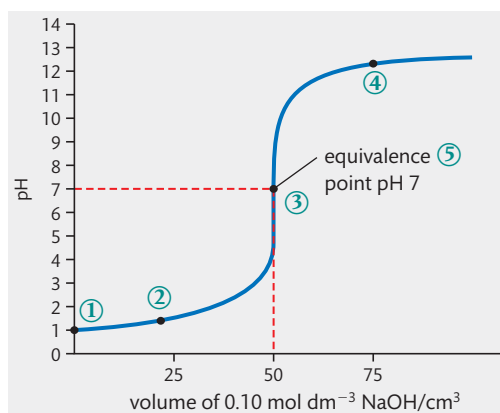

Figure 8.11 Titration curve for strong acid–strong base.

The following points can be deduced from the graph:

1 initial pH = 1 (pH of strong acid);
2 pH changes only gradually until equivalence;
3 very sharp jump in pH at equivalence: from pH 3 to pH 11;

Figure 8.12   Titration curve for weak acid–strong base.

Note that acids and bases react in stoichiometric ratios, irrespective of whether they are weak or strong. In other words equivalence is achieved with the same volume of alkali added to the strong acid, HCl, as to the weak acid, CH_3COOH, given that they are equimolar solutions.
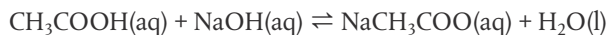
CHALLENGE YOURSELF

3   How can we justify the assumption that [acid] = [HA] and [salt] = [A⁻]? When might this not be a valid approximation to make?
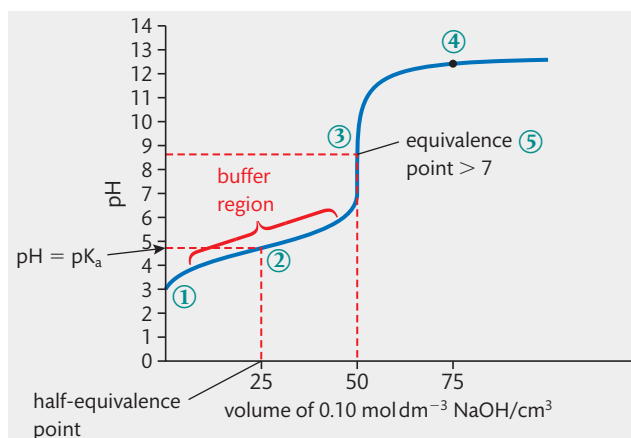
4   after equivalence the curve flattens out at a high value (pH of strong base).

5   **pH at equivalence = 7**.

2   Weak acid and strong base

For example:

$$CH_3COOH(aq) + NaOH(aq) \rightleftharpoons NaCH_3COO(aq) + H_2O(l)$$

• pH at equivalence > 7 as the anion hydrolysis releases OH⁻.

The following points can be deduced from the graph:

1   initial pH fairly high (pH of weak acid);

2   pH stays relatively constant until equivalence – labelled as buffer region;

3   jump in pH at equivalence from about pH 7.0–11.0, which is not as much of a jump as for a strong acid–strong base titration;

4   after equivalence the curve flattens out at a high value (pH of strong base);

5   **pH at equivalence is > 7**.

The reaction mixture after addition of 25cm³ of base is of particular interest. It is labelled as the **half-equivalence** point in the graph as it represents where exactly half of the acid has been neutralized by base and converted into salt, while the other half of the acid in the flask remains unreacted. This mixture, having equal quantities of a weak acid and its salt, is therefore a buffer. This explains why the pH in this region is shown to be relatively resistant to change in pH on the addition of small amounts of base and why it is labelled as the **buffer region** in the graph above.

The pH at the half-equivalence point gives us an easy way to calculate pK_a. Because at this point [acid] = [salt], we can substitute these values into the equilibrium expression of the acid:

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

so if we assume that [acid] = [HA] and [salt] = [A⁻], then [HA] = [A⁻] and so we can cancel these terms in the equilibrium expression:

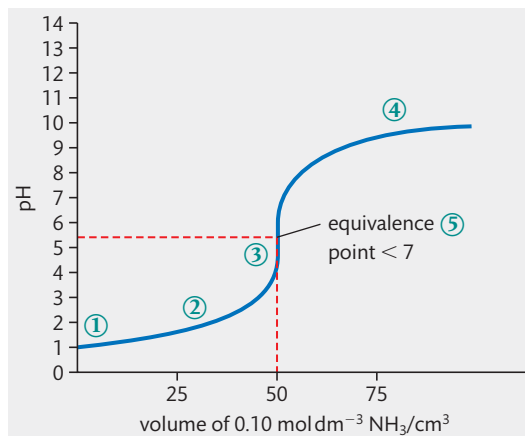$$\therefore K_a = [H^+] \text{ and } pK_a = pH$$

We can read the pH at the half-equivalence point directly from the graph, and so deduce the pK_a of the acid as shown. Note that a parallel calculation of pK_b can be done when a titration is carried out with acid added to base.

3 Strong acid and weak base

For example:

$$HCl(aq) + NH_3(aq) \rightleftharpoons NH_4Cl(aq)$$
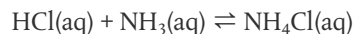
• pH at equivalence < 7 as cation hydrolysis releases H^+.


The following points can be deduced from the graph:

1 initial pH =1 (strong acid);
2 pH stays relatively constant through the buffer region to equivalence;
3 jump in pH at equivalence from about pH 3.0–7.0;
4 after equivalence the curve flattens out at a fairly low pH (pH of weak base);
5 **pH at equivalence is < 7**.

4 Weak acid and weak base

For example:

$$CH_3COOH(aq) + NH_3(aq) \rightleftharpoons NH_4CH_3COO(aq)$$
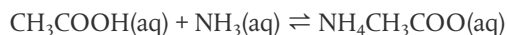
• pH at equivalence is difficult to define.
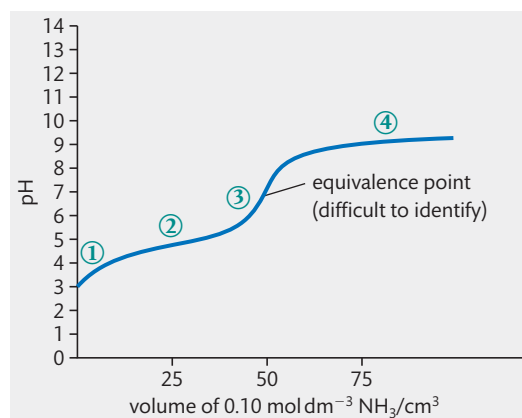
Figure 8.13 Titration curve for strong acid–weak base.

At half equivalence, pH = pK_a or pOH = pK_b.

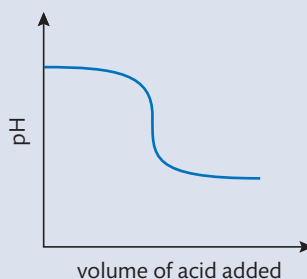**Figure 8.14** Titration curve for weak acid–weak base.

The following points can be deduced from the graph:

1 initial pH is fairly high (pH of weak acid);
2 addition of base causes the pH to rise steadily;
3 change in pH at the equivalence point is much less sharp than in the other titrations;
4 after equivalence the curve flattens out at a fairly low pH (pH of weak base).

This titration does not give a clearly defined equivalence point as there is no significant jump in pH to identify, due to several equilibria being involved. For this combination of acid and base, it is better to use other techniques, such as conductimetric measurements, to determine the equivalence point.

> (!) pH curves can equally well be described in terms of the addition of acid to a base, in which case the curves will be the inverse of those described here.
>
> [Graph: pH on vertical axis, volume of acid added on horizontal axis, showing a curve that starts high and decreases sharply then flattens out]
>
> Be sure to check which way round the data are given when answering questions on this topic. Note that this is the way a titration must be performed to calculate K_b of a weak base.

Exercises

43 Separate 20.0 cm³ solutions of a weak acid and a strong acid of the same concentration are titrated with NaOH solution. Which will be the same for these two titrations?

　I　initial pH
　II　pH at equivalence point
　III　volume of NaOH required to reach the equivalence point

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

44 Sketch a graph for the pH change as 0.1 mol dm⁻³ HCl(aq) is added to 25 cm³ of 0.1 mol dm⁻³ NH₃(aq). Mark on your graph the pH at equivalence and the buffer region.

45 Titration experiments can be used to deduce the pK_a of a weak acid. Taking the neutralization reaction between CH₃COOH and NaOH as an example, show how the pK_a for the acid can be deduced from *two* different points on the titration curve.

Indicators signal change in pH

We learned in section 8.2 that acid–base indicators are substances whose colour depends on the pH of the solution. They therefore signal a change in pH by undergoing a distinct colour change.

These indicators are themselves weak acids or weak bases in which the undissociated and dissociated forms have different colours. If we consider an indicator HIn that is a weak acid, it exists in equilibrium in solution as follows:
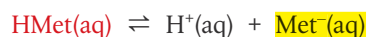
$$HIn(aq) \ \rightleftharpoons \ H^+(aq) \ + \ In^-(aq)$$
colour A　　　　　　　　　　colour B
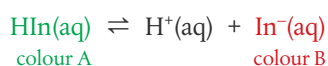
By applying Le Chatelier's principle, we can predict how this equilibrium will respond to a change in the pH of the medium.

- Increasing [H⁺]: the equilibrium will shift to the left in favour of HIn.
- Decreasing [H⁺]: the equilibrium will shift to the right in favour of In⁻.

In other words, at low pH colour A will dominate and at higher pH colour B will dominate.

For example, methyl orange is an indicator that is red when placed in a solution of acid such as HCl. As an alkali is added and the pH increases, the indicator changes to yellow. We can show this in an equation using HMet to represent the weak acid and Met⁻ to represent its conjugate base.

$$\text{HMet(aq)} \rightleftharpoons \text{H}^+\text{(aq)} + \text{Met}^-\text{(aq)}$$

Universal indicator paper showing a range of colours in response to being dipped in solutions of different pH. The light green is neutral, the orange and red are increasingly acidic, whereas the dark green and purple are increasingly alkaline. Universal indicator is made of a mix of indicators so that it changes colour across the pH range. Other indicators change colour at a fixed end-point, as described in this section.

Methyl orange indicator changes colour when added to an acid or alkali. It turns red in acid (left) and yellow in alkali (right).

Indicators change colour when the pH is equal to their pK$_a$

The change in colour of methyl orange, known as its **change point** or **end-point**, happens in the range pH 3.1–4.4. What determines the pH at which this occurs for an indicator?

We can answer this by considering the equilibrium expression for the above reaction.
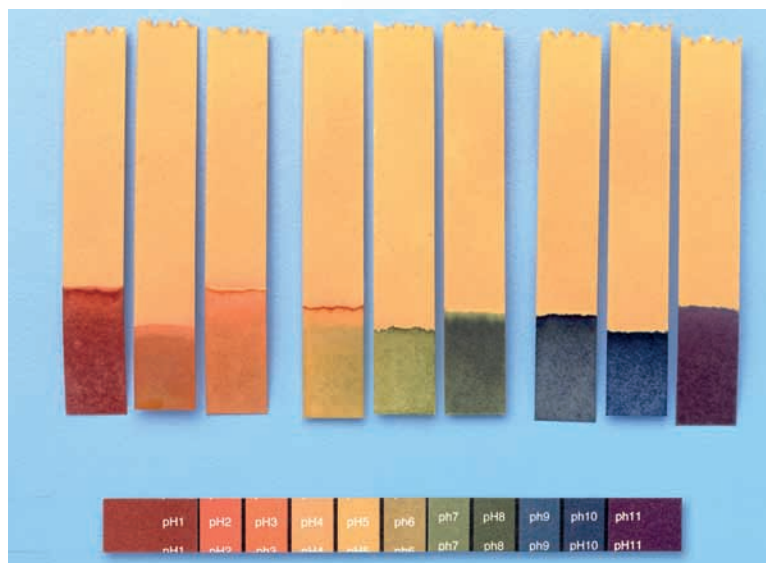
The acid dissociation constant is defined as follows:

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

At the point where the equilibrium is balanced between the acid and its conjugate base, that is where [In⁻] = [HIn], the indicator is exactly in the middle of its colour change. As these values cancel in the equation

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

the expression becomes simplified as $K_a = [\text{H}^+]$ or pK_a = pH.

Indicators are substances that change colour reversibly according to the pH of the solution.

At this point, the addition of a very small volume of acid or base will shift the equilibrium as described above, and so cause the indicator to change colour – this is its end-point. We can see from the equation above that this occurs at the pH equal to the pK_a of the indicator. It follows that different indicators, having different pK values, will have different end-points and so will change colour at different pH values. A selection of indicator end-points is given in section 22 of the IB data booklet.

> **The end-point of an indicator is the pH at which it changes colour. This occurs at the pH equal to its pK_a.**

> Remember that not all indicators change colour at pH 7. Different indicators change colour at a wide range of pH values, from acidic to basic.

> Make sure that you do not confuse the terms 'equivalence point' and 'end-point'.
> • The equivalence point is where stoichiometrically equal amounts of acid and base have neutralized each other.
> • The end-point is the pH at which the indicator changes colour.
> A titration is set up so that the pH of these two points coincides.

Indicators can be used to signal the equivalence point in titrations

Because indicators give us a visible cue when pH changes, they can be used to identify the equivalence points in titrations, given that this is the place where the pH changes most dramatically. An indicator will be effective in signalling the equivalence point of a titration when *its end-point coincides with the pH at the equivalence point*. This means that different indicators must be used for different titrations, depending on the pH at the equivalence point.

The following steps will help you to choose an appropriate indicator for a particular titration.

1   Determine what combination of weak and strong acid and base are reacting together.
2   Deduce the pH of the salt solution at equivalence from the nature of the parent acid and base (page 384).
3   Choose an indicator with an end-point in the range of the equivalence point by consulting data tables.

For example, in the titration of a weak acid with a strong base the equivalence point occurs in the range pH 7–11. An appropriate indicator would therefore be one whose end-point lies in this range, such as phenolphthalein (end-point range 8.2–10.0) as shown in Figure 8.15.
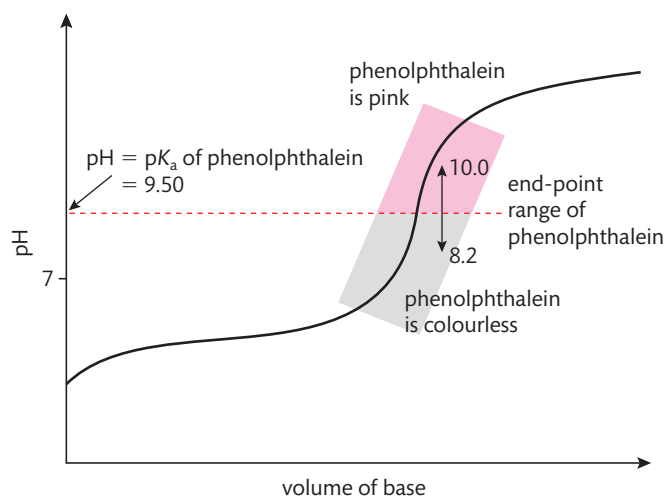

Figure 8.15   A weak acid–strong base titration showing how phenolphthalein will change colour and so effectively signal when equivalence is reached.

The table on page 393 gives examples of suitable indicators for the different titrations.

Reactants in titration	pH range at equivalence	Example of suitable indicators	pK_a	End-point range of indicator and colour change
strong acid + strong base	3–11	phenolphthalein	9.50	8.2–10.0; colourless to pink
		methyl orange	3.46	3.2–4.4; red to yellow
weak acid + strong base	7–11	phenolphthalein	9.50	8.2–10.0; colourless to pink
		phenol red	8.00	6.6–8.0; yellow to red
strong acid + weak base	3–7	methyl orange	3.46	3.2–4.4; red to yellow
		bromophenol blue	4.10	3.0–4.6; yellow to blue
weak acid + weak base	this combination of acid and base does not give a significant change in pH at equivalence, so there is no suitable indicator to use here			

Our eyes are able to identify the distinct colour of one form of an indicator (e.g. HIn) when the ratio of its concentration to that of the other form (In⁻) is about 10:1. So for a transition to be observed from the colour of HIn to the colour of In⁻ at the end-point, the ratio of these concentrations must change from 10:1 to 1:10. This represents a range of two pH units. This is why there is a range of ±1 pH units on either side of the value of pK_a at which the eye can definitely notice the colour change occurring. This is given as the **end-point range** in the table.

When an indicator is used to detect the equivalence point in a titration, a few drops of it are added to the solution in the conical flask at the start of the procedure. As the other solution is added from the burette and the neutralization reaction occurs, the exact volume at which the indicator changes colour can be recorded as the equivalence point. A difference of just one drop of added solution from the burette should produce the dramatic change in colour at this point.

Exercises

46 Which statement about indicators is always correct?

    A   The mid-point of an indicator's colour change is at pH = 7.
    B   The pH range is greater for indicators with higher pK_a values.
    C   The colour red indicates an acidic solution.
    D   The pK_a value of an indicator is within its pH range.

47 Bromocresol green has a pH range of 3.8–5.4 and changes colour from yellow to blue as the pH increases.

    (a) Of the four types of titration shown in the table above, state in which two of these this indicator could be used.
    (b) Suggest a value for the pK_a of this indicator.
    (c) What colour will the indicator be at pH 3.6?

8.5 Acid deposition

Understandings:

- Rain is naturally acidic because of dissolved CO_2 and has a pH of 5.6. Acid deposition has a pH below 5.6.
- Acid deposition is formed when nitrogen or sulfur oxides dissolve in water to form HNO_3, HNO_2, H_2SO_4, and H_2SO_3.
- Sources of the oxides of sulfur and nitrogen and the effects of acid deposition should be covered.

Although all rain water is acidic, the term 'acid rain' only applies to some rain water. How does language as a way of knowing influence communication in science?

Applications and skills:

- Balancing the equations that describe the combustion of sulfur and nitrogen to their oxides and the subsequent formation of H_2SO_3, H_2SO_4, HNO_2, and HNO_3.
- Distinction between the pre-combustion and post-combustion methods of reducing sulfur oxide emissions.
- Deduction of acid deposition equations for acid deposition with reactive metals and carbonates.

Causes of acid deposition

All rain water is naturally acidic owing to the presence of dissolved carbon dioxide, which dissolves in water to form the weak acid carbonic acid, H_2CO_3.

$$H_2O(l) + CO_2(g) \rightleftharpoons H_2CO_3(aq)$$
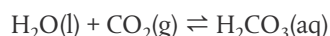
Carbonic acid ionizes to form the following equilibrium:

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$
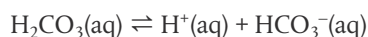
This gives a solution with a minimum pH of 5.6. **Acid rain** refers to solutions with a pH below 5.6, and which therefore contain additional acids. The main contributors to acid rain are the oxides of sulfur and nitrogen, which are primary pollutants. Acid rain is a secondary pollutant produced when these acidic gases dissolve in water.

Acid deposition is a broader term than acid rain and includes all processes by which acidic components as precipitates or gases leave the atmosphere. There are two main types of acid deposition:

- wet acid deposition: rain, snow, sleet, hail, fog, mist, dew fall to ground as aqueous precipitates;
- dry acid deposition: acidifying particles, gases fall to ground as dust and smoke, later dissolve in water to form acids.

Test tubes containing normal rain water (left) and acid rain (right) with universal indicator solution added to show acidity. The normal rain water has a pH of above 5.6, while the acid rain has a lower pH. In this example the pH = 4.0.

Rain water is naturally acidic due to dissolved CO_2. Rain water with a pH < 5.6 is known as acid rain.
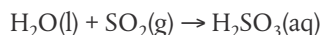
Sulfur oxides

Sulfur dioxide, SO_2, is produced from the burning of fossil fuels, particularly coal and heavy oil in power plants used to generate electricity. It is also released in industrial processes of smelting where metals are extracted from their ores. It is estimated that about 50% of annual global emissions of sulfur dioxide come from coal.

$$S(s) + O_2(g) \rightarrow SO_2(g)$$
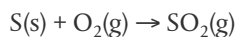
Sulfur dioxide is a colourless gas with a sharp smell. It dissolves in water to form sulfurous acid, $H_2SO_3(aq)$.

$$H_2O(l) + SO_2(g) \rightarrow H_2SO_3(aq)$$

Sulfur dioxide can also be oxidized to sulfur trioxide, SO_3, which then dissolves in water to form sulfuric acid, H_2SO_4.

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

$$H_2O(l) + SO_3(g) \rightarrow H_2SO_4(aq)$$
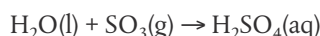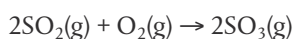
There are several mechanisms that might occur in these reactions, and the chemistry is complex given the wide range of conditions and other chemicals found in the atmosphere. During sunlight hours photo-oxidation may occur, and oxidation may also be catalysed by tiny particles of metal present in the clouds, such as iron or manganese. Ozone (O_3) or hydrogen peroxide (H_2O_2) present as pollutants in the atmosphere, can be involved. A more detailed study involves hydroxyl free radicals, •HO, which form by reactions between water and atomic oxygen or ozone. A free radical possesses an unpaired electron and so is a short-lived and reactive species. It is shown with the symbol •.

$$\bullet HO + SO_2 \rightarrow \bullet HOSO_2$$

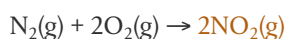$$\bullet HOSO_2 + O_2 \rightarrow \bullet HO_2 + SO_3$$
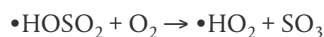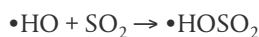
Nitrogen oxides

Nitrogen monoxide, NO, is produced mainly from internal combustion engines, where the burning of the fuel releases heat energy that causes nitrogen and oxygen from the air to combine.

$$N_2(g) + O_2(g) \rightarrow 2NO(g) \qquad \Delta H = +181 \text{ kJ mol}^{-1}$$

A similar reaction gives rise directly to the brown gas, nitrogen dioxide, NO_2.

$$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$$

Nitrogen dioxide also forms from the oxidation of nitrogen monoxide:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$
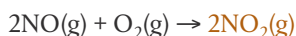
Nitrogen dioxide dissolves in water to form a mixture of nitrous acid (HNO_2) and nitric acid (HNO_3).

$$H_2O(l) + 2NO_2(g) \rightarrow HNO_2(aq) + HNO_3(aq)$$

Alternatively, nitrogen dioxide can be oxidized to form nitric acid.

$$2H_2O(l) + 4NO_2(g) + O_2(g) \rightarrow 4HNO_3(aq)$$

Figure 8.16 The formation of acid deposition.

Figure 8.16 The formation of acid deposition.

SO$_2$ and NO$_x$ are carried into the atmosphere

Oxidation and hydrolysis produce H$_2$SO$_3$(aq), H$_2$SO$_4$(aq), HNO$_2$(aq) and HNO$_3$(aq)

Acid clouds form which can travel 1500 km from source

Runoff

Leaching

Dry deposition

Local wet deposition (by rain, snow and fog)

> Several other oxides of nitrogen exist, and the term NO$_x$ is used somewhat variably. But in atmospheric chemistry it refers specifically to the total of the two oxides of nitrogen NO and NO$_2$ present.

> One of the most controversial aspects of acid deposition is that its effects often occur far from the source of the pollutants, due to atmospheric weather patterns. In many cases, this means countries are suffering the impact of other countries' industrial processes. Legislation to reduce the impact of acid deposition has therefore been the subject of intense political debate, and several international protocols have developed. These have led to significant reductions in sulfur emissions in many countries, but reduction in nitrogen oxide emissions has been less effective.

These reactions also proceed via different mechanisms, depending on the conditions and chemical cocktail in the atmosphere. Photo-oxidation, the presence of ozone, and hydroxyl free radicals (•HO) all contribute to the production of nitrous acid and nitric acid.

$$\bullet HO + NO \rightarrow HNO_2$$
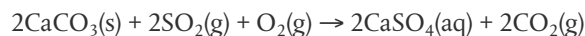$$\bullet HO + NO_2 \rightarrow HNO_3$$

In summary, a complex set of reactions in the atmosphere converts the primary pollutants SO$_2$ and NO into acid rain. The main active components of acid rain are H$_2$SO$_3$(aq), H$_2$SO$_4$(aq), HNO$_2$(aq), and HNO$_3$(aq).
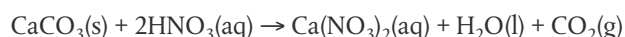
Effects of acid deposition

Impact on materials

The building materials marble and limestone are both forms of calcium carbonate, CaCO$_3$. Both sulfur dioxide (in dry deposition) and sulfuric acid (in acid rain) react with this, forming the calcium salt, CaSO$_4$:

$$2CaCO_3(s) + 2SO_2(g) + O_2(g) \rightarrow 2CaSO_4(aq) + 2CO_2(g)$$

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

As calcium sulfate is somewhat more soluble than calcium carbonate, it washes out of the limestone or flakes off. Calcium sulfate has a greater molar volume than calcium carbonate, so its formation causes expansion and stress in the stonework. A similar reaction occurs with nitric acid, forming the soluble nitrate salt:

$$CaCO_3(s) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + H_2O(l) + CO_2(g)$$

These reactions all lead to erosion of structures, and many historic buildings and statues have suffered in this way.

Acid deposition also affects metals, causing corrosion. Again components of both dry deposition and acid rain react with metals such as iron, forming the salt. This enables

ionic conductivity to occur, which leads to an increase in the rate of electrochemical corrosion reactions such as rusting:

$$Fe(s) + SO_2(g) + O_2(g) \rightarrow FeSO_4(s)$$
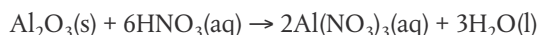
$$Fe(s) + H_2SO_4(aq) \rightarrow FeSO_4(aq) + H_2(g)$$
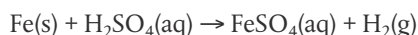
In addition, acid rain is able to react with and so remove the protective oxide layer on the surface of metals such as aluminium:

$$Al_2O_3(s) + 6HNO_3(aq) \rightarrow 2Al(NO_3)_3(aq) + 3H_2O(l)$$

As a result, acid rain causes significant damage to metallic structures such as bridges, rail road tracks, and vehicles.

> You should be able to write equations for the reactions between the different components of acid rain and reactive metals and metal carbonates, similar to those developed in section 8.2. Note though that nitric acid, HNO_3, does not react as a typical acid releasing hydrogen from metals, as it is an oxidizing agent and releases NO instead. (So in fact this reaction releases more pollutant into the air to form more acid rain.)

Impact on plant life

Acid rain has been shown to be a direct cause of slower growth, injury, or death of plants. One of its effects is to cause important minerals such as Mg^{2+}, Ca^{2+}, and K^+ held in the soil to become soluble and so wash away in a process called **leaching**, before they can be absorbed by plants. Without sufficient Mg^{2+} ions, for example, a plant cannot synthesize chlorophyll and so cannot make its food through photosynthesis. At the same time, acid rain causes the release of substances that are toxic to plants, such as Al^{3+}, which damage plant roots. In addition, dry deposition can directly affect plants by blocking the pores for gas exchange, known as stomata. Forests in hilly regions seem to be particularly vulnerable because they tend to be surrounded by acidic clouds and mists. Some of the worst effects on forests have been in Europe, though the impact is seen worldwide.

Impact on water

Acid rain has caused a number of lakes to become 'dead' – unable to support life. Many fish including trout and perch cannot survive at pH values below 5. Below pH 4, rivers are effectively dead as toxic Al^{3+} ions normally trapped in the rock as insoluble aluminium hydroxide leach out under acid conditions:

$$Al(OH)_3(s) + 3H^+(aq) \rightarrow Al^{3+}(aq) + 3H_2O(l)$$
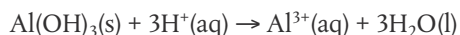
Aluminium ions interfere with the operation of the fish's gills and reduce their ability to take in oxygen.

Acid rain also contributes to an additional problem known as **eutrophication**. This is over-fertilization of bodies of water, and can be caused by nitrates present in acid rain. It results in algal blooms leading to oxygen depletion, and sometimes the death of the lake or stream.

Impact on human health

Acid rain does not directly affect human health but its components can react to form fine sulfate and nitrate particles that can travel long distances and be present in inhaled air. These particles irritate the respiratory tract and increase the risk of illnesses such

▲ Marble statue damaged by acid rain.

▲ Woodland devastated by the effects of acid rain in the Czech Republic, near the border with Germany. This is one of the most affected areas in Europe.

as asthma, bronchitis, and emphysema. They can also cause irritation to the eyes. The release of toxic metal ions such as Al^{3+}, Pb^{2+}, and Cu^{2+} by the reaction of acid rain on metal structures such as pipes is also a potential health risk.

Responses to acid deposition

The link between increasing industrialization causing atmospheric pollution and acid rain was first described in Manchester, England, in 1852. However, the phenomenon did not gain widespread attention until the 1970s when some of the impacts described above became evident in several countries. As a result, many governments responded with measures aimed to reduce the emissions of nitrogen and sulfur oxides. Some of these are summarized below.
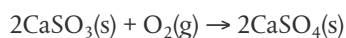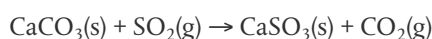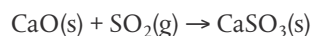
Reduction of SO_2 emissions

i) Pre-combustion methods

These are processes that reduce or remove the sulfur present in coal or oil before combustion. Where the sulfur is present as a metal sulfide, it can be removed by crushing the coal and washing with water. The high density metal sulfide sinks to the bottom and so separates from the clean coal. **Hydrodesulfurization** (HDS) is a catalytic process that removes sulfur from refined petroleum products by reacting it with hydrogen to form hydrogen sulfide, H_2S. This is a highly toxic gas, so it is captured and later converted into elemental sulfur for use in the manufacture of sulfuric acid, H_2SO_4.

ii) Post-combustion methods

Flue-gas desulfurization can remove up to 90% of SO_2 from flue gas in the smoke stacks of coal-fired power stations before it is released into the atmosphere. The process uses a wet slurry of CaO and $CaCO_3$ which reacts with SO_2 to form the neutral product calcium sulfate, $CaSO_4$.

$$CaO(s) + SO_2(g) \rightarrow CaSO_3(s)$$

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

$$2CaSO_3(s) + O_2(g) \rightarrow 2CaSO_4(s)$$

The calcium sulfate has industrial uses such as making plasterboard.

Reduction of NOx emissions

i) Catalytic converters in vehicles

Exhaust gases can be controlled by the use of catalytic converters in which the hot gases are mixed with air and passed over a platinum- or palladium-based catalyst. The reaction converts toxic emissions into relatively harmless products. For example:

$$2CO(g) + 2NO(g) \rightarrow 2CO_2(g) + N_2(g)$$
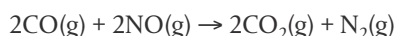
ii) Lower temperature combustion

As mentioned in Chapter 7, the formation of nitrogen monoxide is reduced at lower temperature. Recirculating the exhaust gases back into the engine lowers the temperature to reduce the nitrogen oxide in the emissions.

NATURE OF SCIENCE

Acid deposition has been recognized as a problem for over a century, but it was not until there was convincing evidence for the long-range transport of pollutants that it became a subject of international concern in the 1970s. Intense scientific research into the formation and impacts of acidic rainfall then led to policy responses at the national and local level. Environmental issues like this are almost always global in nature, but the responses must be tackled at source locally. Scientists need to make the public aware of their findings so that corrective actions are understood, and individuals can make informed lifestyle choices.

Other options

In addition to finding ways to reduce the emission of the primary pollutants when fossil fuels are burned, other solutions to the problems of acid deposition include lowering the demand for fossil fuels. More efficient energy transfer systems, greater use of public transport, and switching to renewable energy sources are all part of this.

The restoration of ecosystems damaged by acid rain is a long-term process. One method is to use calcium oxide (CaO), known as lime, or calcium hydroxide ($Ca(OH)_2$) to neutralize the acid.

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

$$Ca(OH)_2(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + 2H_2O(l)$$
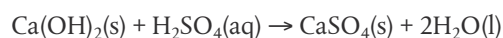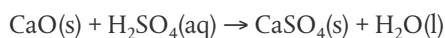
Response to acid rain in Sweden. The dosing column is adding $Ca(OH)_2$ to the stream, to help neutralize the acidity of the water.

Exercises

48 (a) Explain why natural rain has a pH of around 5.6. Give a chemical equation to support your answer.

(b) Acid rain may be 50 times more acidic than natural rain. One of the major acids present in acid rain originates mainly from burning coal. State the name of the acid and give equations to show how it is formed.

(c) The second major acid responsible for acid rain originates mainly from internal combustion engines. State the name of this acid and state two different ways in which its production can be reduced.

(d) Acid rain has caused considerable damage to buildings and statues made of marble ($CaCO_3$). Write an equation to represent the reaction of acid rain with marble.

(e) State three consequences of acid rain.

(f) Suggest a method of controlling acid rain, not involving a chemical reaction, for reducing sulfur dioxide emissions from power stations.

49 The table gives some substances found in air.

Name	Formula
sulfur dioxide	SO_2
nitrogen monoxide	NO
particulates	–

(a) Identify the pollutant(s) which contribute(s) to acid rain.

(b) Identify the pollutant(s) which come(s) mainly from power stations.

(c) The presence of one of these pollutants makes the ill effects of the others worse. Identify the pollutant and explain why it has this effect.

(d) Emissions of one of these pollutants have been controlled by reaction with calcium oxide. Identify this pollutant and write an equation for the reaction with calcium oxide.

(e) Identify the pollutants that come primarily from motor vehicles and describe the basis for their production.

50 (a) Describe the difference in dispersion between dry acid deposition and wet acid deposition.

(b) Explain the physical and chemical processes involved in the development of wet acid deposition.

51 Identify the free radical involved in the formation of sulfuric acid and nitric acid in acid rain and explain how it is formed.

Practice questions

1 The K_b value for a base is 5.0×10^{-2} mol dm^{-3} at 298 K. What is the K_a value for its conjugate acid at this temperature?

 A 5.0×10^{-2} **B** 2.0×10^{-6} **C** 2.0×10^{-12} **D** 2.0×10^{-13}

2 Which combination will form a buffer solution?

 A 100 cm^3 of 0.10 mol dm^{-3} hydrochloric acid with 50 cm^3 of 0.10 mol dm^{-3} sodium hydroxide

 B 100 cm^3 of 0.10 mol dm^{-3} ethanoic acid with 50 cm^3 of 0.10 mol dm^{-3} sodium hydroxide

 C 50 cm^3 of 0.10 mol dm^{-3} hydrochloric acid with 100 cm^3 of 0.10 mol dm^{-3} sodium hydroxide

 D 50 cm^3 of 0.10 mol dm^{-3} ethanoic acid with 100 cm^3 of 0.10 mol dm^{-3} sodium hydroxide

3 Equal volumes and concentrations of hydrochloric acid and ethanoic acid are titrated with sodium hydroxide solutions of the same concentration. Which statement is correct?

 A The initial pH values of both acids are equal.

 B At the equivalence points, the solutions of both titrations have pH values of 7.

 C The same volume of sodium hydroxide is needed to reach the equivalence point.

 D The pH values of both acids increase equally until the equivalence points are reached.

4 Bromophenol blue changes from yellow to blue over the pH range of 3.0 to 4.6. Which statement is correct?

 A Molecules of bromophenol blue, HIn, are blue.

 B At pH < 3.0, a solution of bromophenol blue contains more ions, In$^-$, than molecules, HIn.

 C The pK_a of bromophenol blue is between 3.0 and 4.6.

 D Bromophenol blue is a suitable indicator to titrate ethanoic acid with potassium hydroxide solution.

5 What is the K_b expression for the reaction of ethylamine with water?

 A $K_b = [CH_3CH_2NH_3{}^+]\,[OH^-]$

 B $K_b = \dfrac{[CH_3CH_2NH_3{}^+][OH^-]}{[CH_3CH_2NH_2]}$

 C $K_b = \dfrac{[CH_3CH_2NH_3{}^+][H_2O]}{[CH_3CH_2NH_2]}$

 D $K_b = [CH_3CH_2NH_2]\,[H_2O]$

6 pK_w for water at 10 °C = 14.54. What is the pH of the pure water at this temperature?

A 6.73 **B** 7.00 **C** 7.27 **D** 7.54

7 What is K_b for the aqueous fluoride ion given that K_w is 1.0×10^{-14} and K_a for HF is 6.8×10^{-4} at 298 K?

A $\dfrac{1}{6.8 \times 10^{-4}}$

B $(6.8 \times 10^{-4})(1.0 \times 10^{-14})$

C $\dfrac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}}$

D 6.8×10^{-4}

8 If 20 cm^3 samples of 0.1 mol dm^{-3} solutions of the acids below are taken, which acid would require a different volume of 0.1 mol dm^{-3} sodium hydroxide for complete neutralization?

A nitric acid **B** sulfuric acid **C** ethanoic acid **D** hydrochloric acid

**9** Which mixture of acid and alkali would produce a buffer solution?

	Acid	Alkali
A	40 cm^3 0.1 mol dm^{-3} HCl	60 cm^3 0.1 mol dm^{-3} NaOH
B	60 cm^3 0.1 mol dm^{-3} HCl	40 cm^3 0.1 mol dm^{-3} NaOH
C	40 cm^3 0.1 mol dm^{-3} HCl	60 cm^3 0.1 mol dm^{-3} NH$_3$
D	60 cm^3 0.1 mol dm^{-3} HCl	40 cm^3 0.1 mol dm^{-3} NH$_3$

10 Ammonia acts as a weak base when it reacts with water. What is the K_b expression for this reaction?

A $\dfrac{[NH_4^+][OH^-]}{[NH_3][H_2O]}$ **B** $\dfrac{[NH_3][H_2O]}{[NH_4^+][OH^-]}$ **C** $\dfrac{[NH_3]}{[NH_4^+][OH^-]}$ **D** $\dfrac{[NH_4^+][OH^-]}{[NH_3]}$

11 The indicator HIn is used in a titration between an acid and base. Which statement about the dissociation of the indicator, HIn, is correct?

$$HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$$
$$\text{colour A} \qquad\qquad\qquad \text{colour B}$$

A In a strongly alkaline solution, colour B would be observed.

B In a strongly acidic solution, colour B would be observed.

C [In$^-$] is greater than [HIn] at the equivalence point.

D In a weakly acidic solution colour B would be observed.

12 Which salt dissolves in water to form an acidic solution?

A ammonium nitrate **C** potassium chloride

B sodium ethanoate **D** sodium hydrogencarbonate

13 Which of the following mixtures of equimolar solutions produces a buffer with pH < 7 at 298 K?

A 50 cm^3 HCl(aq) and 150 cm^3 NH$_3$(aq)

B 50 cm^3 CH$_3$COOH(aq) and 50 cm^3 HCl(aq)

C 100 cm^3 CH$_3$COOH(aq) and 50 cm^3 NaOH(aq)

D 50 cm^3 CH$_3$COOH(aq) and 50 cm^3 NH$_3$(aq)

**14** Hypochlorous acid, HOCl(aq), is an example of a weak acid.

  (a) State the expression for the ionic product constant of water, K_w.   (1)

  (b) A household bleach contains sodium hypochlorite, NaOCl(aq), at a concentration of 0.705 mol dm^{-3}. The hypochlorite ion, OCl$^-$(aq), is a weak base.

$$OCl^-(aq) + H_2O(l) \rightleftharpoons HOCl(aq) + OH^-(aq)$$
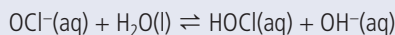
    (i) The pK_a value of HOCl(aq) is 7.52. Determine the K_b value of OCl$^-$(aq) assuming a temperature of 298 K.   (1)

    (ii) Determine the concentration of OH$^-$(aq), in mol dm^{-3}, at equilibrium and state **one** assumption made in arriving at your answer other than a temperature of 298 K.   (3)

    (iii) Calculate the pH of the bleach.   (2)

(Total = 7 marks)

15 (a) (i) Define the terms *acid* and *base* according to the Brønsted–Lowry theory. Distinguish between a weak base and a strong base. State **one** example of a weak base.   (3)

    (ii) Weak acids in the environment may cause damage. Identify a weak acid in the environment **and** outline **one** of its effects.   (2)

    (iii) The graph below indicates the pH change during the titration of 20.0 cm^3 of 0.100 mol dm^{-3} of CH$_3$COOH(aq) with 0.100 mol dm^{-3} KOH(aq). From the graph, identify the volume of KOH(aq) and the pH at the equivalence point.   (2)
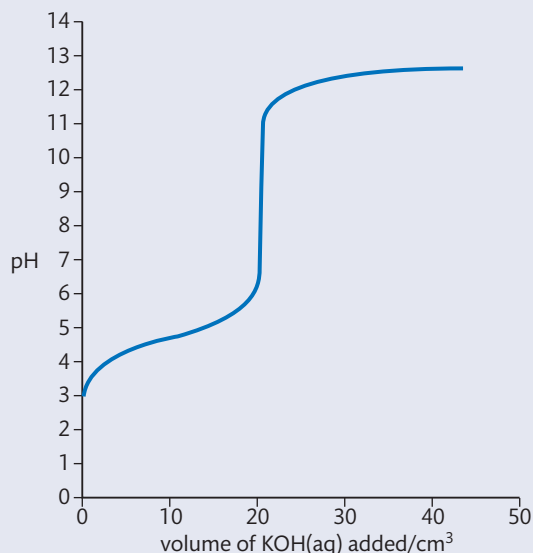
    (iv) Explain how the graph could be used to determine the pK_a of ethanoic acid **and** determine the pK_a value for these data.   (2)

    (v) Sketch a graph, similar to the previous graph, to indicate the change in pH during a titration of 25.0 cm^3 of 0.100 mol dm^{-3} HNO$_3$(aq) with 0.100 mol dm^{-3} OH$^-$(aq). On your graph, clearly indicate the starting pH value, the equivalence point, the pH at the equivalence point, and the final pH reached.   (4)

  (b) (i) Describe how an indicator works.   (3)

    (ii) Using Table 16 of the Data Booklet, identify the most appropriate indicator for the titration of ethanoic acid with potassium hydroxide. Explain your choice.   (2)

(Total = 18 marks)

16 Ammonia can be converted into nitric acid (HNO_3(aq)) and hydrocyanic acid (HCN(aq)). The pK_a of hydrocyanic acid is 9.21.

(a) Distinguish between the terms *strong acid* and *weak acid* and state the equations used to show the dissociation of each acid in aqueous solution. (3)

(b) Deduce the expression for the ionization constant, K_a, of hydrocyanic acid and calculate its value from the pK_a value given. (2)

(c) Use your answer from part (b) to calculate the [H^+] and the pH of an aqueous solution of hydrocyanic acid of concentration 0.108 mol dm^{-3}. State **one** assumption made in arriving at your answer. (4)

(*Total = 9 marks*)